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PLYBOND CHEMISTRY FOR MULTIPLY BOARD

Master´s Programme in Chemical, Biochemical and Materials Engineering
Major in Fibre and Polymer Engineering

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Tiivistelmä

Pakkauskartonkien kulutus on kasvanut merkittävästi ja samaten kiertokuidun ja matala tiheyksisen kemi-hierteen (CTMP) käyttö pakkausmateriaalina, tarkoituksenä säästää ymäristöä ja tehostaa materiaalien käyttöä. Riittävä kerrostenvälinen z-suuntainen lujuus on vaikea toteuttaa ja kiertokuidun heikentyvä laatu sekä kemi-hierteen entistäkin alhaisempi tiheys vaikeuttaa lujuuden saavuttamista entisestään.

Työn tavoitteena oli luoda luotettava laboratoriomittakaavainen monikerroskartonkien valmistustapa käyttäen uusimpia, kerrosten välistä lujuutta parantavia tekniikoita. Sekä taivekartongin että lainerin valmistusta testattiin dynaamisella arkkimuotilla. Samanaikaisesti testattiin erilaisia lujuuspolymeereja etsien parasta kerrostenvälistä lujuutta parantavaa yhdistelmää.

Taivekartongin kerrosten väliin ruiskutettiin veteen sekoitettua keittämätöntä natiivia maissitärkkelystä, johon oli sekoitettu joko anionista, kationista tai amfoteerista lujuuspolymeeriä. Arkkien lujutta testattiin mittaamalla z-lujuus ja arkkien poikkileikkeet kuvannettiin, jotta saatiin todistettua tärkin asettuminen kerrosten rajapintaan. Tulokset osoittivat, että monikerroskartonkia oli mahdollista valmistaa uudella menetelmällä, mutta arkintekoon kuluva aika saattoi olla liian pitkä. Tulokset osoittivat, että spray-tärkki itsessään parantaa jonkin verran lujuutta. Amfoteerisen polymeerin, spray-tärkin ja kationisen massatärkin yhdistelmällä lujuus parani jopa 23 % referenssiin verrattuna. Kuvantamalla saatiin todistettua tärkkipartikkeleiden sijoittuminen kerrosten rajapintaan. Myös anionineen lujuuskemikaali paransi merkittävästi lujuutta kun tärkin määrä kaksinkertaistettiin.

Kiertokuidusta valmistetun lainerin pintakerrosten väliin ruiskutettiin vesikerros, joka koostui jauhetusta massasta, kationisesta tärkistä sekä anionisesta, kationisesta tai amfoteerisesta lujuuspolymeeristä. Lujuus testaattin mittaamalla z-lujuus, puhkaisulujuus sekä puristuslujuus (SCT). Tulokset osoittivat, että jauhettu massa yksinään parantaa huomattavasti Z-suuntaista lujuutta, anionisen kemikaalin lisätessä tätä vaikutusta. Z-lujuuden parantuminen ei tapahtunut muiden lujuusominaisuusien kustannuksella. Myös puhkaisu- ja puristuslujuus paranivat jonkin verran. Tässä tutkimuksessa tärkkimäärän nosto näkyi anionisen polymeerin tehoa nostavana tekijänä, vaikka lujuuspolymeerien varauksien suuruudella ei havaittu olevan johdonmukaista merkitystä.

Avainsanat Kuivalujuus; laineri; spray-tärkki; vesikerros; taivekartonki

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Abstract of master's thesis

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Abstract

The consumption of multiply packaging boards has vastly increased. To save environment and materials, the consumption of recycled fibers and low-density CTMP has grown at the same time. However, recycled fibers are poor in quality. Especially Z-directional tensile between plies is difficult to improve and lower quality fibers address more challenges. The aim of the thesis was to establish reliable way to make multiply sheets in laboratory environment, using the latest z-directional strength improving techniques. Both folding boxboard (FBB) and testliner sheets were formed with dynamic sheet former (DSF). At the same time, the best performing plybond chemistry was under study.

A nonionic spray starch was introduced between top/middle and middle/bottom plies of FBB. Anionic, amphoteric and cationic strength chemicals were tested in the spray starch. Z-strength was tested, and the retention of starch granules was observed microscopically. The study showed, that multiply sheets including spray layer were possible to form, but the time-consuming forming of several layers needs some alteration. Results revealed, that the spray starch alone promotes strength in some extent. The strength of FBB was improved by 23 % with combination of spray starch, low amount of cationic starch and amphoteric polymer carrying relatively low anionic charge. Starch granules were detected between layers. Also, anionic chemical was found to improve strength when sufficient amount of cationic starch was added into the pulp.

An aqualayer consisting of refined pulp, cationic starch and cationic, anionic or amphoteric strength chemical was introduced between testliner plies. Testliner was tested for burst, short span compression SCT and Z-strength. It was seen that refined pulp had strength improving tendency. Anionic strength chemistry was found to improve the z-strength of testliner even further. The burst strength and SCT of testliner were also improved. Increase in starch was observed to improve the performance of the anionic polymers, but generally, the charge of the strength chemical was not dictating property.

Keywords Dry strength; spray; aqualayer; testliner

Preface

This thesis was executed at Kemira Espoo R&D Center during Jan- Aug 2018. I would like to thank Kemira Oyj and the whole organization for supporting my wishes to take my studies further to this point.

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And my family. I sincerely thank you, dear children Riku and Linnea, for keeping up the spirit at home. And to my dear husband Jouni; without your support, sacrifices and efforts at home we would not be at this point. Thank you all.

Espoo 05.09.2018

Jaana Laine

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Indications

A	[m^2]	area
b	[Nm^{-2}]	shear bond strength per unit area
D	[kg/m^3]	density
E	[N/m^2]	modulus of elasticy
F	[N]	force
I		the moment of inertia of the sample
P	[m]	fiber perimeter
S	[N*m]	stiffness
T	[$N\ m\ kg^{-1}$]	long zero-span
W	[g/m^2]	basis weight
Z	[$N\ m\ kg^{-1}$]	short zero-span
σZD	[kPa]	maximum tensile stress
ρ	[$kg\ m^{-3}$]	fiber density
λ	[m]	mean fiber length

Abbreviations

A-PAM	Anionic acrylamide
BCT	Box compression strength
FBB	Folding boxboard
CCT	Corrugated crush test
CD	Cross direction
CMT	Concora Medium Test
C-PAM	Cationic acrylamide
CTMP	Chemi-thermomechanical pulp
DLVO	Derjaguin- Landau- Verwey-Overbeek
ECT	Edge compression strength
MD	Machine direction
NaCl	Sodium chloride
PEM	Polyelectrolyte multilayer
PGW	Pressure groundwood
PNVF	Poly-N-vinyl formamide
PVF	Polyvinyl formamide
PVAm	Polyvinyl amine
RCT	Ring crush test
rds	Retention, drainage, strength
RBA	Relative bonded area
RMP	Refined mechanical pulp
rpm	Revolutions per minute
SCTMP	Semi-chemi-thermo-mechanical pulp
SEM/EDS	Scanning Electron Microscope/ Energy Dispersive X-ray Spectroscopy Analysis
SGW	Stone groundwood
SFO	Sheet fed off-set
TMP	Thermomechanical pulp
vdW	van der Waals

1 INTRODUCTION

As consumers increasingly purchase products online, the demand for packaging boards has also continued to grow. There lies a modest contradiction between the increased production rates of packaging materials and the movement for environmental awareness. In 1987 the World Commission on Environment and Development defined sustainability. According to the statement, the term sustainability refers to "*economic development activity that meets the needs of the present without compromising the ability of the future generations to meet their own needs*" (Portney, 2015). The paper and board industry has answered to this dilemma by developing lighter, stronger and recyclable materials. Light weighting of board is a concept, that delivers all parties from board manufacturers to end user's positive results throughout the products life circle. Lighter products result in savings through material and transport costs. Since all corrugated board is counted as recyclable board packaging material (Kirwan, 2013), it has great positive influence on the carbon footprint of the packaging materials.

These positive outcomes come with a counter side, since decreased grammage ultimately challenges the strength properties of the material. Bulky boards have significantly fewer fibers, and hence less bonded area. Already Brown (1937) showed in his study, that ply strength has great influence on the board strength. Decrease in bonding sites gives greater role and pressure to the bonding between plies. Also, the converting processes e.g. folding and printing with increased speed subject the surface to various forces. Forces, which the plies must be able to resist to certain extent.

The effect of the role of dry strength additives and starch has been widely studied (Pettersson, 2006[ab]; Lee, 2007) and the theory behind the ply strength is well documented (Brown, 1937; Carambassis & Rutland, 1999). Nevertheless, the range of furnishes is very wide. Studies with virgin fiber based furnishes can be more straightforward. But the case is different with recycled fibers, when the origin, quality and excess chemicals present make the evaluation more demanding. Hence, there is

still great deal of open questions concerning the optimized amount and combination of chemicals with altering furnishes.

The aim of the literature review is to clarify the chemistry behind the tested application. Furthermore, the methodology behind the applications are presented.
The literature review starts with a brief product analysis, followed by demands for mechanical performance and the most essential properties of folding boxboard and test liner. Review continues with surface and colloid chemistry, clarifying the forces affecting polymer adsorption and the mechanics of dry strength development. The spray rheology and aqualayer headbox related applications are then discussed.

The purpose of experimental part is to establish a suitable and reliable method for preparing multiply sheets in laboratory scale. At the same time the aim is to optimize the Z-directional strength in both virgin fiber and RCF based multiply boards. This is tested by combining starch and dry strength polymer chemistry. Performance of anionic, cationic and amphoteric dry strength additives will be evaluated through mechanical performance and starch retention. The role of wet web dryness is mainly discussed in the literature part, but it is also lightly evaluated in the experimental part. The used methodology is based on patented applications, which are presented in the literature review. The focus of the experimental part will be on the interactions of starch and dry strength polymers.

LITERATURE PART I

2 PRODUCT ANALYSIS

Among all packaging papers multiply boards create the base of packaging materials. The application and end use divide boards into three main categories: carton boards, container boards and specialty boards. The packaging industry also categorises packaging into primary, secondary and tertiary forms based on its functions which are presented in *table 1*. The original purpose of the packaging boards is mainly to preserve the products, protect those during transport and handling, provide needed information and finally make the appearance attractive and sellable for the consumer (Kuusipalo & Taipale, 1998; Emblem, 2012)

Table 1. The functions of different level packaging (Emblem, 2012)

Packaging level	*Function*
Primary	Provides information, preserves the products from light, moisture and oxygen, visual appearance.
Secondary	Stacks consumer packages together, provides information, protects primary packaging during transport and piling.
Tertiary	Protects goods from physical stress and dirt during transport,

These core tasks dictate the necessary properties the packaging boards must provide in different stages of its life circle. In this study folding boxboard (FBB) presents example for carton boards in primary and secondary packaging. Test liner is part of the containerboards group and is an example of tertiary packaging., Test liners are used to manufacture corrugated and solid fibre board. (Holik, 2006; Emblem, 2012; Kirwan, 2013)

2.1 Folding box board

Cartonboards come in several grades, in which the thickness, basis weight, pulp origin and possible coating vary. Different pulps give different characteristics to the board and consequently every cartonboard grade has different combination of pulps. Folding boxboard is typically built out of three layers, but the multilayer structure of boards can vary from one to even seven layers, where different pulp layers form the board and each layer gives the board unique properties. In FBB, mechanical pulp is used in middle layer to get affordable bulky structure. Mechanical pulp can be stone ground wood (SGW), pressure ground wood (PGW), refined mechanical pulp (RMP), thermo-mechanical pulp (TMP) or chemi-thermomechanical pulp (CTMP). Among mechanical pulps CTMP has the lowest number of fines. Top and bottom layers are bleached chemical pulp which give the board stiffness and brighter appearance. (Joukio & Mansikkamäki, 1998) Solid unbleached board (SUB) is used in liquid packaging applications where high puncture and tear strength are essential features. *Figure 1* demonstrates some of the variations of cartonboard grades. Usually the top, bottom or both surfaces are coated with mineral-pigment to achieve smooth and good surface for printing. (Kirwan, 2013; Ek et al., 2009)

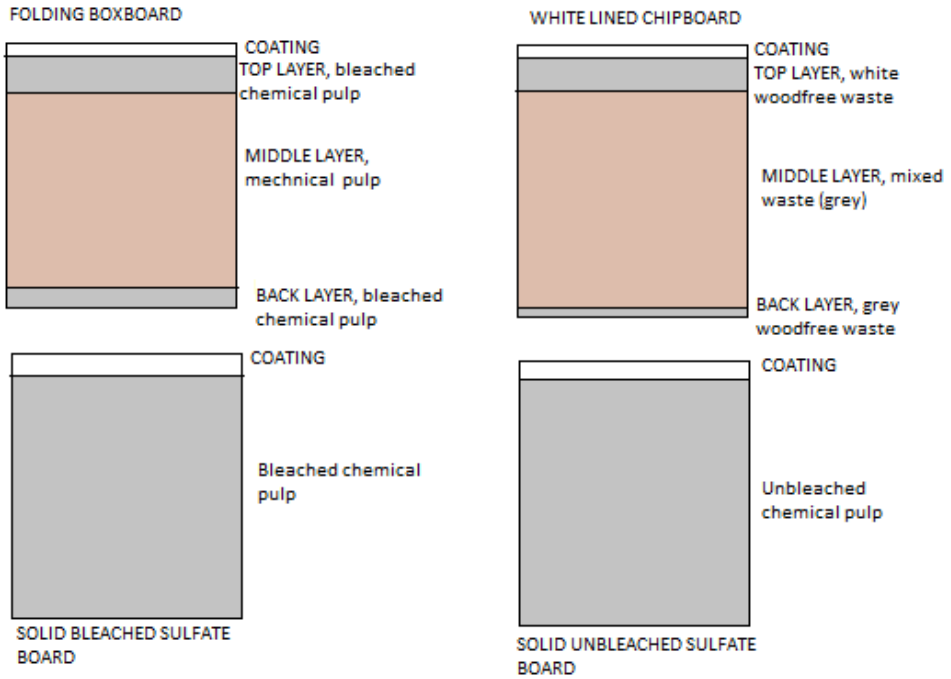

Figure 1. Cross section of Cartonboard grades (modified Joukio & Mansikkamäki, 1998).

2.2 Testliner and fluting

Liner and fluting are the base components to fabricate corrugated board. Kraft liner is a paper with basis weight between 100 and 400 g/m². When the recycled corrugated board material content of liner exceeds 60 % it is categorized as testliner. Corrugated board has a sandwich - like multilayer structure, where liner and the fluting medium are glued together. Materials can be recycled, virgin origin or of combination of those. These days most fluting is made of recycled fibers. Virgin material used is SCTM processed because it gives shorter fibers, which are suitable for corrugating. (Kirwan, 2013; Ek et al., 2009)

The purpose of the structure has the same principal as in composites. The unique properties of different layers are combined, and the resulting corrugated board has greater strength properties than the single components alone. *Figure 2* demonstrates the different structure combinations of corrugated board. The purpose of fluting is to give strength and support to the structure of corrugated boards. To provide all this it needs to have stiffness and elasticity. Liner instead needs to have good surface strength and smoothness for printing. Roughness on the bottom side is good for gluability when the corrugated board is manufactured. It is also the main surface to reject puncture. Structure of corrugated board can vary from one single face to triple wall. The increasing number of layers gives the board higher resistance to bending.

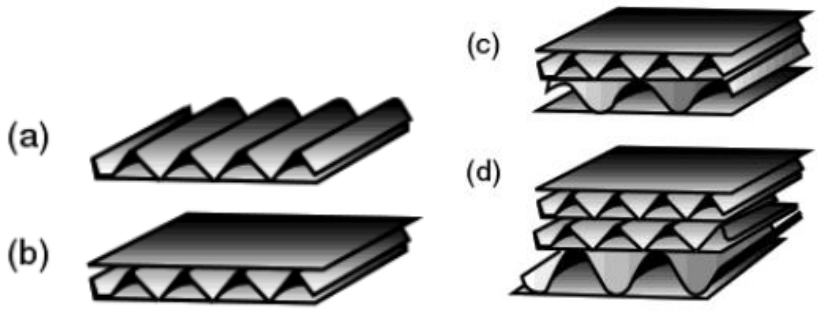

Figure 2. Single face (a), single wall (b), double wall (c), and triple wall (d) structures (Kirwan, 2013).

The structure of fluting is also carefully considered. The pitch and height of the flute have great influence on the strength properties of the corrugated board. Flutes have five different heights which are labelled A, B, C, D and F in the order they were invented. (Kirwan, 2013; Ek et al., 2009)

2.2.1 Strength properties of multiply boards

The strength of the board is a combination of multiple variants. It is a question of the physical structure of the paperboard, origin of fibres, number of fines and the chemical bonding of the fibres. The strength of individual fiber is defined as fiber strength, which is measured by zero -span. Zero means, that the distance between the measuring clamps is practically zero or near it. (Sundblad, 2015; Lehto, 2004) The strength of the paper is seen as a combination of the strength of individual fibers and the interfiber bonding of the fibers in paper. These are the key factors which influence on the tensile strength of the paper sheet. Page (1969) introduced an equation, where the tensile strength was presented through fibre properties, as seen in equation (1). (Anson, 2006)

$$\frac{1}{T} = \frac{9}{8Z} + \frac{12A\rho}{bP\lambda\, RBA}, \quad (1)$$

where

T	is	long zero-span (N m kg^{-1})
Z	"	short zero-span (N m kg-1)
A	"	fiber cross sectional area (m²)
ρ	"	fiber density (kg m^{-3})
b	"	shear bond strength per unit area (Nm^{-2})
P	"	fiber perimeter (m)
λ	"	mean fiber length (m)
RBA	"	relative bonded area

In equation (1) RBA refers to sheet properties and is rather difficult to measure experimentally. Therefore, indirect measurement of scattering has been used to determine the extent of bonding (Batchelor, 2006). Furthermore, the behavior of the fibers in the paper network during paper making has also effect on the combination. Pulps have different characteristics which are dependent on the pulping method, the chemical composition of the fibers and the physical appearance of the fibers.
Mechanical pulp has shorter and stiffer fibers with tube like appearance. Because of the stiff nature, fibers have less bonds between each other. Therefore, the formed paper has lower density and bulk. (Ek et al., 2009; Bierman, 1996; Vainio & Paulapuro, 2007)

Fibers in chemical pulp are collapsed and more flexible making the conforming with each other much easier. This results in increased bonding sites between the fibers. The level of refining has effect on the strength. In general, the more fibrillation and fines there are, the more bonding area is available. Increased bonding area increases interfiber bonding and furthermore improves properties, such as tensile and burst. However, when refining is taken to extent the strength of individual fibers decreases. As a result, properties which are dependent on fiber strength decrease. (Ek et al., 2009; Bierman, 1996)

Interfiber bonding can be measured either directly or indirectly. Direct measurements include mechanical testing, such as peel test where the whole sheet is evaluated, z-toughness test, wheel delamination test and Scott Bond, which is the most commonly used test for measuring z-directional strength. (Fellers et al., 2012) Among the most important strength properties for packaging boards are tensile, burst, tear, z-directional strength, compression strength and surface strength. (Coffin, 2011) The mechanical properties are stronger in MD direction (Biermann, 1996)

2.2.2 Properties of folding box board and test methods

The testing and evaluation of the performance of folding boxboard is mainly based on its mechanical performance. The strength of the multilayer structure is investigated thoroughly. The mechanical properties tend to be dependent on the measurement direction of the paper, machine direction (MD) having stronger properties than cross direction (CD). (Kirwan, 2013)

Z-directional strength

The most important feature of the board is the strength between layers, because the Z-directional strength is known to be the weakest link in the board structure. As mentioned, board is subjected to the z-directional load in many processes e.g. during printing, folding and creasing. Z-directional failure is found in the thickness direction of the board (Coffin, 2011) The failure originates from the weakness of the interfiber bonding, when the z-directional strength of the paper is exceeded. The failure occurs in the sheet, not on the surface of the paper. (Fellers et al., 2012)

The z-directional strength is not equivalent to the surface strength of the board (Coffin, 2011) Z- directional strength e.g. delamination tendency, is traditionally measured with dynamic Scott Bond method (Fellers et al., 2012). This method is based on

measuring the force needed to delaminate the board when the sample is confronted with impact from front of the sample. As shown in *figure 3*, the board is pressed between adhesive tape and attached to a L-shape metal bracket. The pendulum is set free to make a swing. The stored potential energy is at maximum when the pendulum reaches the bracket. The loss of potential energy at the impact is measured, hence the energy needed for delamination is calculated from the moment pendulum passes the bracket. (Koubaa & Kouran, 1995; Fellers et al., 2012)

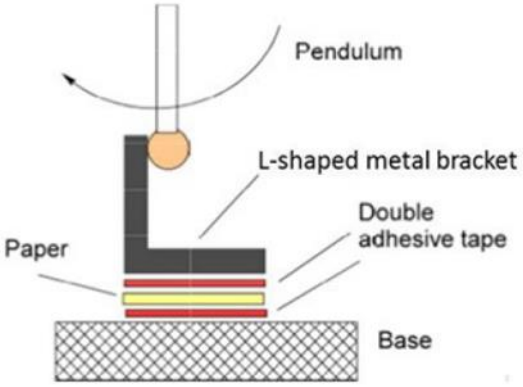

Figure 3. The schematic of Scott Bond measurement (Fellers et al., 2012).

The result of Scott Bond is calculated as energy unit towards the sample area. The method is very sensitive to the orientation of fibers (MD/CD/Z-direction), and it is not very accurate (Mäkinen, 2018) Furthermore, according to Koubaa & Koran (1995) the Scott Bond energy is affected by the basis weight of the sample.

Another popular method is to measure Z-strength, which measures the maximum force sample can resist. In this case the sample is again pressed between adhesives, but the stress is loaded perpendicular to plane (SCAN-P 90:03). When the clamps are separated, the maximum tensile force needed to break the sample is measured. *Figure 4* illustrates the moment when sample starts to delaminate.

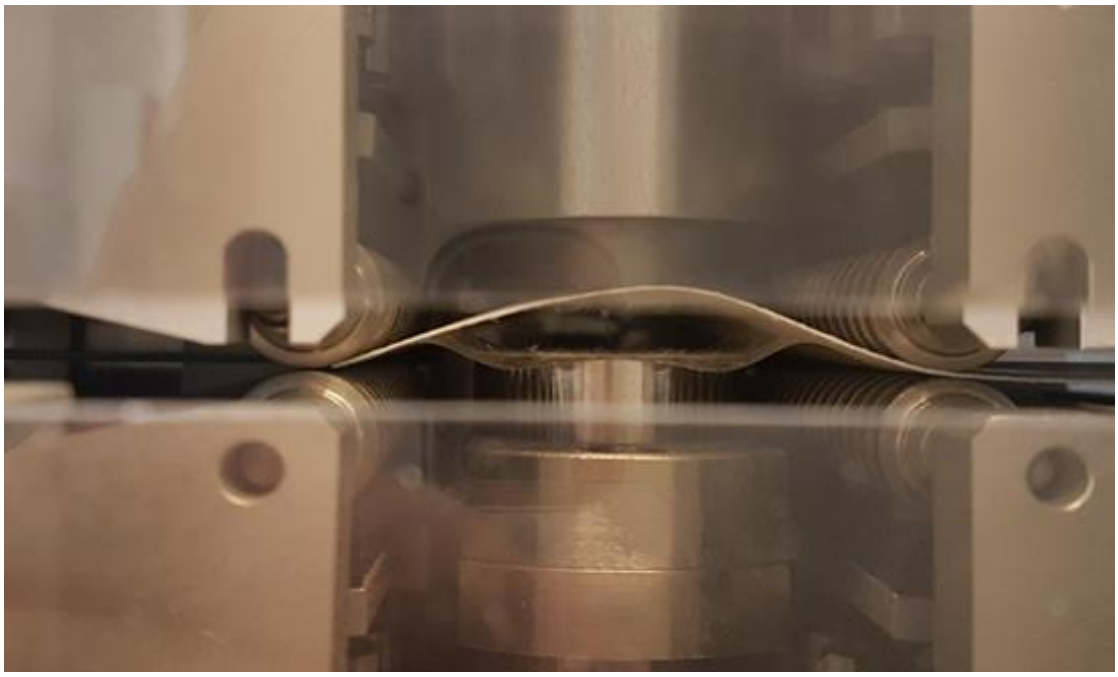

Figure 4. Illustration of sample delaminating during z-strength measurement.

The maximum force which the sample can withstand without delaminating is calculated using equation (2),

$$\sigma_{ZD} = \frac{F}{A} * 10^3, \quad (2)$$

where

σ_{ZD}	is	maximum tensile stress (kPa)
F	"	mean maximum tensile force (N)
A	"	area of the tester platens (mm^2)

In general, these methods are found to correlate well. According to Koubaa & Koran, (1995) the methods correlate, but their focus is different. They stated that considering Scott Bond of thicker samples, the energy lost in the fiber network must be considered along with the delamination energy. Then again, Z-strength includes only the failure energy of interfiber bonding. (Koubaa & Koran, 1995) Also Karlström &Hill (2012) found that the level of gained values was different with small and high energies. Stronger papers had higher Scott Bond values possibly due to higher loading rate (Karlström & Hill, 2012).

Bending stiffness

Bending stiffness is a measure of resistance when the sample faces externally loaded force. It can be measured with more than one method varying from the most common two-point method to four-point method. In a two-point method (*Figure 5, a*) the sample strip is attached firmly from one end and the free end is forced to bend to certain angle, 7.5° or 15° (Levlin, 1999). Notable is, that measuring heavy weight boards with 2-point method may cause damage to the samples, which is seen in decreased stiffness values (Kirwan, 2013). Method can be used with boards if restrictions are taken in consideration, assuring appropriate length-thickness ratio of the sample, and small enough bending angle (Levlin, 1999; Kirwan, 2013). The measuring itself should be conducted in both maschine direction (MD) and cross direction (CD), since the fibre orientation has great effect on the bending stiffness values. Machine direction has clearly higher stiffness, and therefore, it is reasonable to express stiffness as MD/DC ratio. (Kirwan, 2013)

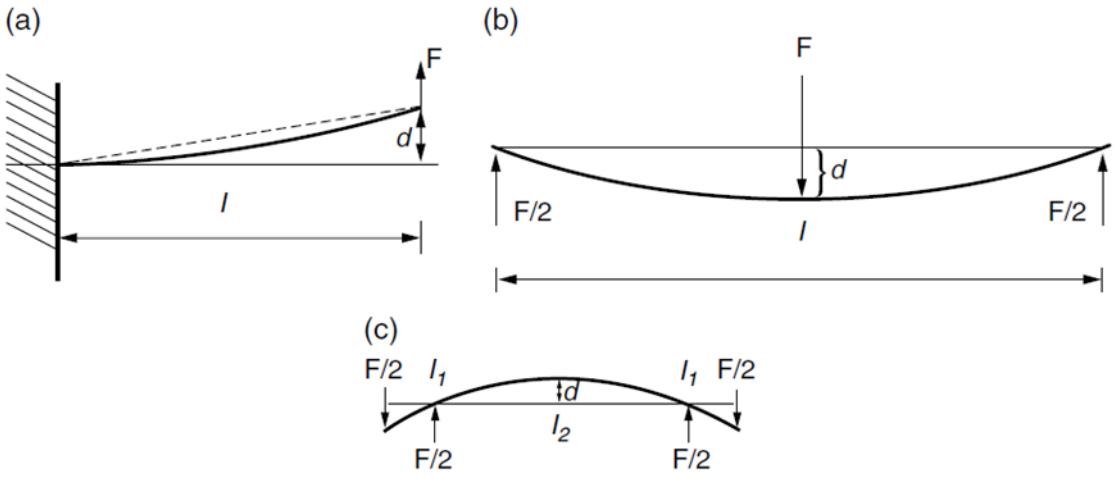

Figure 5. Illustrations of a) two-point, b) three-point c) four-point loading methods used in stiffness measuring (Kirwan, 2013).

From equation (3), one can see how stiffness is dependent on the modulus of elasticy (E) and thickness of the sample (h). Flexural stiffness can be modified by keeping either the basis weight or thickness constant. (Koran & Kamdem, 1989)

$$S=\frac{EI}{b}=\frac{Eh^3}{12}=\left(\frac{E}{D^3}\right)*\left(\frac{W^3}{12}\right), \quad (3)$$

where

S is stiffness (N*m)

E	“	modulus of elasticy (N/m^2)
I	“	the moment of inertia of the sample ($I=bh^3/12$)
h	“	thickness of the sample (m)
b	“	the width of the sample (m)
D	“	density (D=W/h)
W	“	basis weight

The flexural stiffness has great influence on many mechanical properties, such as box compression, creasability, foldability and overall toughness, and runnability of the web (Kirwan, 2007; Kirwan, 2013). In multiply boards stiffness is gained by structural composition, where mechanical and chemical pulp are layered in sandwich like manner (Emblem, 2012). In a multiply board the upper layers bend and give strength to the board, while the bulky middle layer needs to compress (Kirwan, 2013; Koran &Kamdem, 1989). The stiffness of multiply board is a sum of stiffness of all plies involved (Levlin, 1999).

In addition to the production parameters, the stiffness of multiply board is governed by the choice of pulp, thickness and density of the sheet and moreover, the ratio of basis weight between outer layers and middle layer of the board (Koran & Kamdem, 1989). Navaee-Ardeh (2007) developed a model where bending stiffness could be predicted based on theoretical model.

As illustrated in *figure 6,* this indicates, that the share of mechanical pulp in the middle layer can be increased to 75 % and still gain the same stiffness as in commercial three -ply boards with more modest share of mechanical pulp (Navaee- Ardeh, 2007). This is very beneficial from the economical aspect.

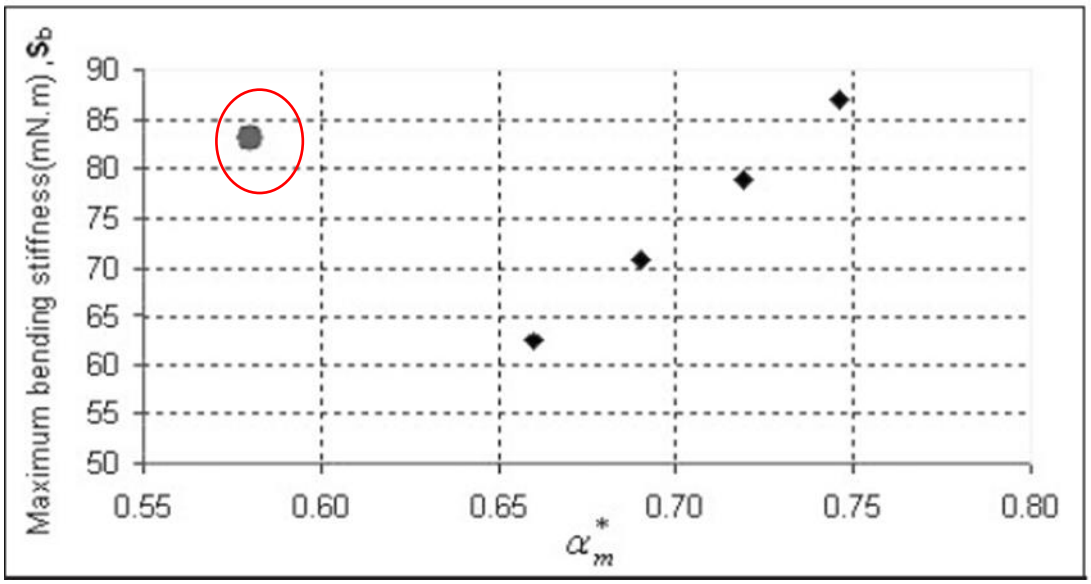

Figure 6. Maximum bending stiffness vs. middle layer basis weight share. Red circle marks the reference point with 58 % middle layer share, effect is tested with four different basis weight shares. (Navaee &Ardeh, 2007)

According to Navaee-Ardeh's (2007) findings, mainly the share of middle layer grammage has effect on elastic modulus when symmetric three-ply board is considered. *Figure 7* illustrates, that the effect of chemical pulp decreases dramatically when the number of plies decrease.

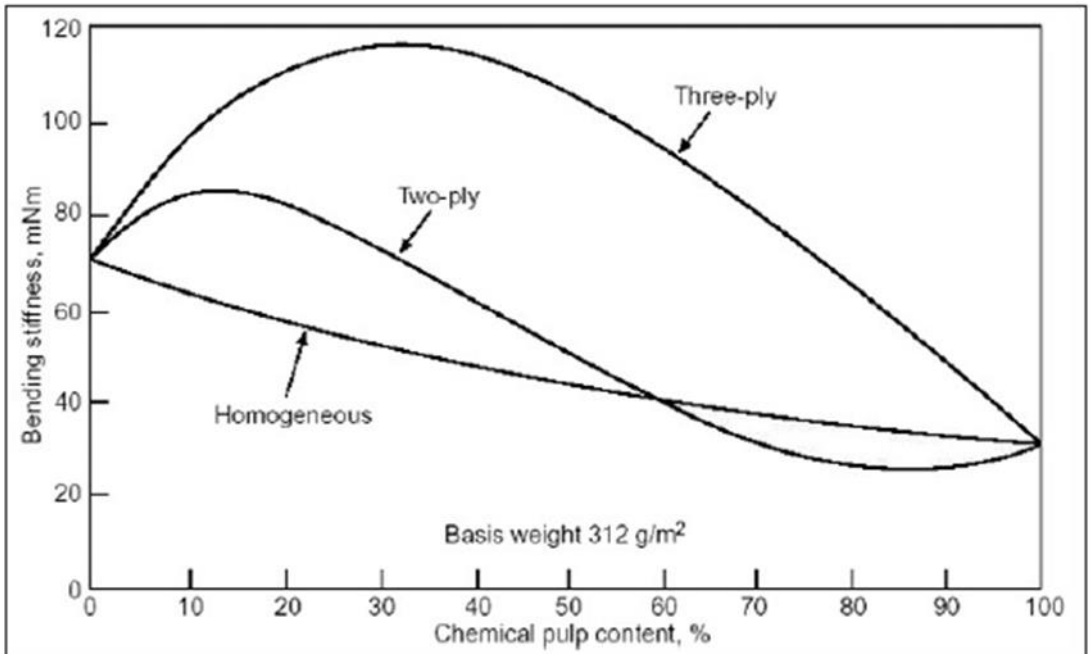

Figure 7. Calculated bending stiffness vs. the share of chemical pulp (Navaee-Ardeh, 2007).

Smoothness

Smoothness is a measure of surface roughness or lack of it. It can be measured with several instruments Parker Print Surf (PPS) being the most common. All smoothness measuring devices are based on air leak between the measured surface and the measuring head.

As a property, smoothness is a visual factor, because it has great influence on the printability of the board. Smoothness is controlled by use of fillers, surface sizing, water-based coating layers and calandering. The choice of pulp has effect on structure and hence the smoothness. Bleached chemical pulps and short fibers are known to give superior surface smoothness. (Kirwan, 2013; Emblem, 2012)

Surface strength

Surface strength of the board is an important factor when the board is converted into product. Surface strength is improved through surface sizing, coating and calendaring. The surface is challenged when inadequate fixing of fillers or fines causes dusting during printing. The dust piles up on the printing rolls and over the time it starts to damage the paper surface (Holik, 2013) Usually the strength is evaluated by dry pick test, which measures the ability of paperboard to resist picking during offset printing. IGT method is rather common. In the method ink tack forces the paper follow the cylinder. *Figure 8* illustrates how oil creates a pulling action on the paper surface, like offset ink, resulting in picking, blistering, or both. (Kirwan, 2013)

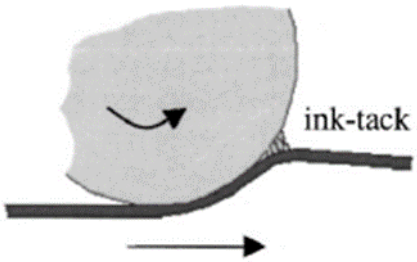

Figure 8. Effect of ink tack in printing (Stenberg, et al. 2001).

2.2.3 Properties of liner

Short Span Compression (SCT_{CD})

The principal failure modes of corrugated board are buckling and compression (Coffin, 2011). Optimum tolerance can be evaluated by mathematical modelling, based on SCT or ring crush test (RCT) measurement (Shallhorn, et al., 2004; Šarčević et al.,

2016). Since RCT tends to give unreliable results with low grammage products (Kirwan, 2013), the SCT_{CD} is found to be more accurate than other compressive testing methods. In RCT the failure origins from both compression and buckling, which is not optimum situation when compression only is under evaluation. The lower the grammage, the greater is the effect on buckling emphasizing it more than necessary. The distinguished differences of the SCT compared to other measuring methods is shortness of the compression span and the way test piece is attached from both ends of the strip (Kainulainen & Söderhjelm, 1999) as illustrated in the *figure 9*. The span is rather short, just 0,7 mm. The unwanted buckling is prevented because there are two sets of clamps moving towards each other. (Kainulainen & Söderhjelm, 1999; Šarčević et al., 2016)

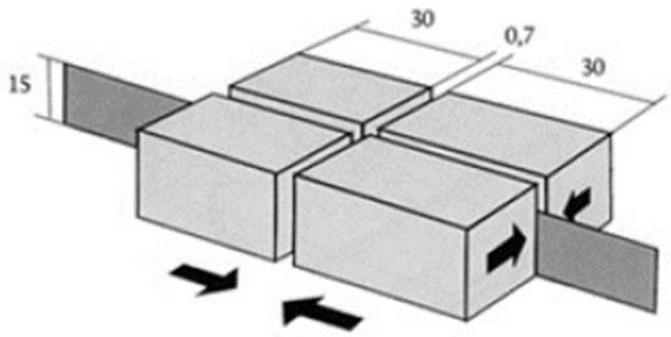

Figure 9. Principle of the SCT test set up (Šarčević et al., 2016).

SCT together with stiffness are used for calculations, when the total performance of the box is evaluated. The sheet density is known to have a close relationship to compression strength. (Coffin, 2011)

Burst

Burst strength is a measure to evaluate the quality of corrugated box (Kirwan, 2013) The value obtained stands for the maximum pressure the board can resist. The burst property has some connection to tensile and elongation of the board. (Levlin, 1999)

It is convenient to express the strength as index, since basis weight has great influence on the burst strength, and this way it is taken in consideration within the results. Burst property can be affected with choice of the pulp and starch addition. Sizing improves burst strength with greater efficiency than adding starch into pulp. (Tutus et al., 2017)

2.2.4 Strength properties of fluting

SCT_{CD}

Since the box strength is a property of the whole panel, the SCT is a crucial property also for fluting. Fluting is an element, that gives strength for stacking and resistance to crushing., it should support the liner boards during loading. (Coffin, 2011)

Concora Medium Test (CMT_{MD})

CMT measures the crushing resistance of the fluting. Fluting consisting of specific number of flutes is made with special fluting apparatus. *Figure 10* illustrates, how the flutes are forced with apparatus and fixed with adhesive tape. (Applied Paper Technology Inc., 2017)

Figure 10. Preparation of fluting (Applied Paper Technology In., 2017)

Test specimen is loaded in the machine direction and the maximum force sustained by a test piece is recorded and expressed in Newtons. (Kainulainen &Söderhjelm, 1999) Test can be done immediately, but it is more convenient to wait 30 minutes and allow the sample condition after being treated with heat. (Kirwan, 2013)

2.3 Requirements of mechanical performance

The paperboards are subjected to various conditions and stresses before reaching the consumer. The converting process itself challenges the board during folding, creasing and printing. Usually paperboards are being printed using either gravure, flexo or sheet fed off-set (SFO) printing method. Especially SFO printing challenges the strength properties of board. The SFO printing speed has increased during recent years and the ink used has very high viscosity at low shear rates. As shown in *figure 11*, the board is subjected to stress from all direction during printing. When approaching the nip (a), the board is subjected to tensile stress. When it is between the rolls (b), compressive stress in included. As paper continues to run, the ink is split

(c) causing interlaminar stresses to the paper or board. (Stenberg & Fellers, 2001; Coffin, 2011)

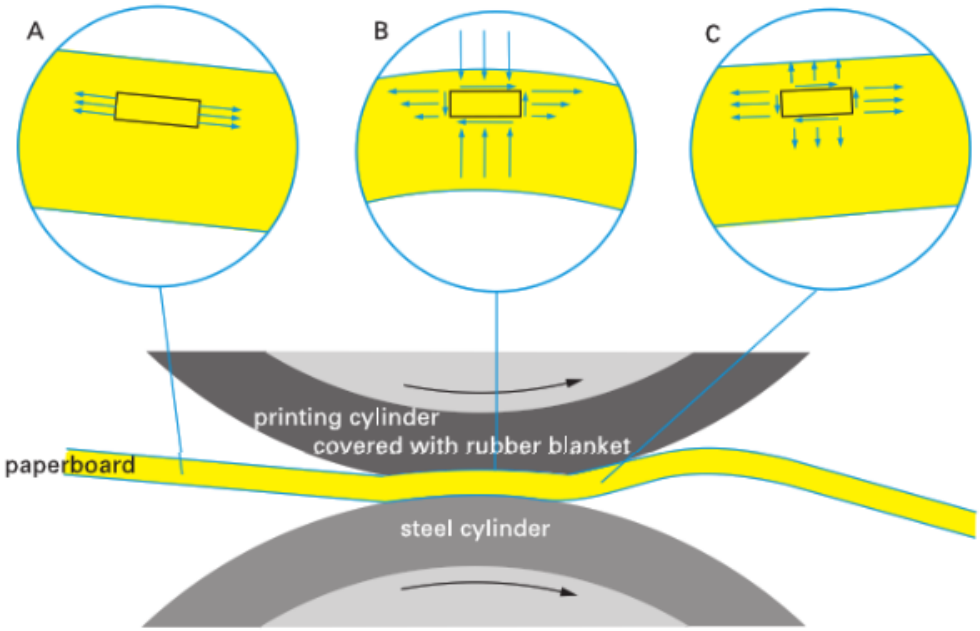

Figure 11. Behavior of paper under printing nip (Coffin, 2011).

These factors can cause inner delamination or blistering during printing, because the force at the delaminating interface is proportional to ink tack. Delamination can occur during printing or during creasing and folding. it can vary from small visible bubbles on the surface to delaminating strips. (Vähä-Nissi et al., 2013)

While trying to make the board as strong and light as possible, these is a limit when some of the converting processes are considered. To get well finished and appealing package the board should always be creased before folding, this decreases possibility of cracking when folded. It is desirable, that the strength between plies is strong enough to succeed during printing. However, plies must open in a controllable manner during creasing and folding. (Kirwan, 2013)

Figure 12 illustrates, how the board is subjected to compression in perpendicular direction to the surface, tensile and shearing strain when creased. Tensile strains are greatest in the surface and reverse side linear plies.

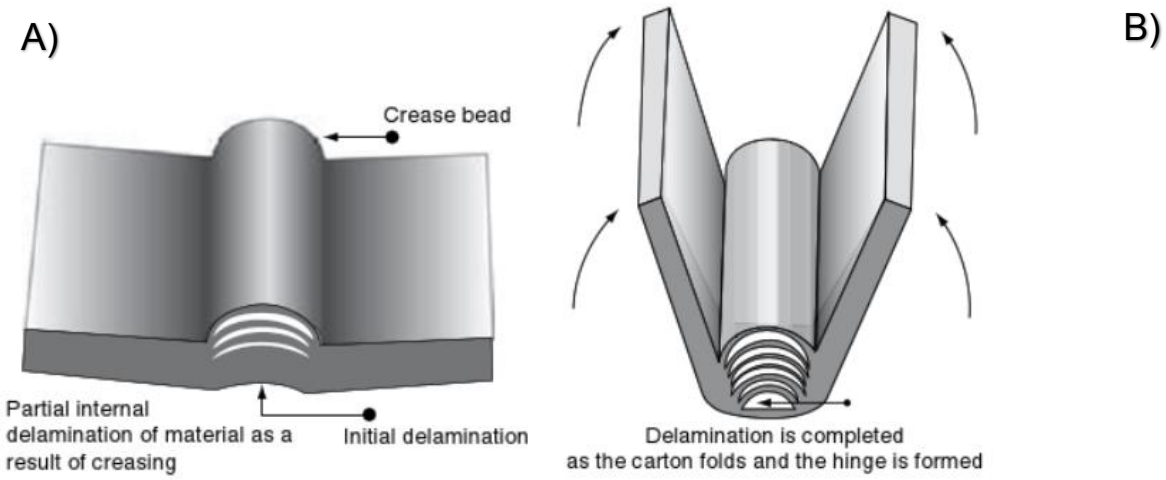

Figure 12. Delamination of board after creasing (a) and folding(b) (Kirwan, 2013).

The surface and coating layers of the board must be strong. Thickness and grammage are board properties which rule the selection of creasing tools. In optimal crease, the paperboard should delaminate into as many thin layers as possible as demonstrated in figure (Kirwan, 2013)

In secondary and tertial packaging compression strength is a critical property. Boxes are piled up on top of each other during transport as illustrated in *figure 13*, and severe loadings are subjected to the package from multiple directions.

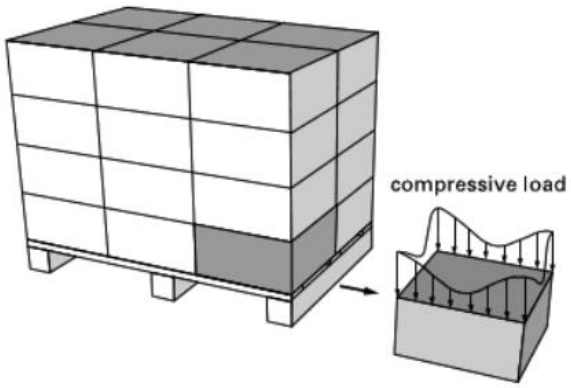

Figure 13. Illustration of compression load during storage and transportation (Coffin, 2011).

3 PLYBOND CHEMISTRY

In this chapter, the interfacial phenomena are discussed. This includes surface and colloid chemistry, which considers the forces between fibers and electrolyte. Additionally, the mechanics of dry strength development are discussed. The interfacial phenomena are based on the fact, that cellulosic fibers are colloids with large area versus unit and most of the interaction take place on particle surfaces. (Eronen, 2011) The concept of bonding in paper originates to the tendency of cellulose molecules to bond to each when the solid content of paper is increases during drying. Strength in paper originates from interfiber bonding and bonding between the fibers. Interfiber bonding is a result of covalent hydrogen bonds, ionic bonds, intermolecular van der Waals forces (vdW) and cellulose molecules entangled with each other. In short, when two fibers are brought in close contact during drying, a phenomenon known as *Campbell Effect* takes place. The surface forces pull fibers together as the amount of water reduces, and gradually other forces take control as interfiber bonding takes place. The surface forces together with mechanical interlocking of fibrils (Schmied et al., 2013) result in attractive vdW forces between the fibers. It is obvious that increase of beating, and thus increased number of fines, will increase the effect of mechanical interlocking (Eronen, 2011; Roberts, 1996; Vainio & Paulapuro, 2007)

To enhance the interfiber bonding, polyelectrolyte additives are added into stock or board surface. Next subchapters will give a brief overlook on the most essential forces and how the adsorption of electrolytes contribute on paper strength.

3.1 Bonding in cellulosic systems

During water removal, the surface tension brings fibers get in close contact with each other. At 25 % solids the surface tension becomes dependent on the thickness of water layer increasing the differential pressure between surfaces. With the contribution of water bridges, the noncovalent hydrogen bonds can form between cellulose hydroxyl groups (Przybysz, 2016; Roberts, 1996) Formation of hydrogen bonds is illustrated in the *figure 14.* The distance between fibres needs to be very modest, since the length of hydrogen bond is rather short. The hydrogen bonds are thought to form when wet web solids content reaches 10-15 %. The distance between bonding hydroxyl groups is only 0,26 nm (Przybysz, 2016)

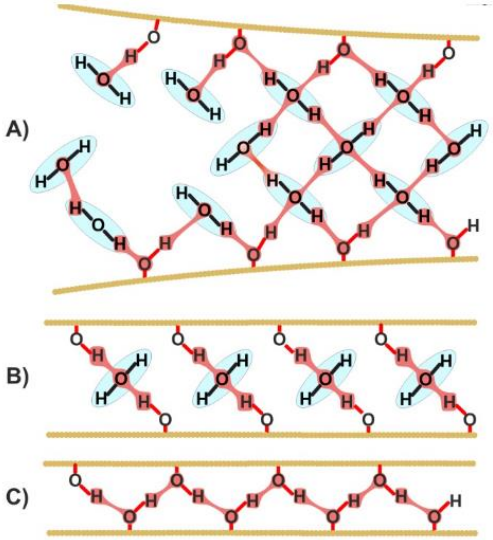

Figure 14. The three steps of hydrogen bond formation (Przybysz, 2016).

3.2 Adsorption of polyelectrolytes and the electrical double layer

Since synthetic strength polymers are relatively costly, it is reasonable to try to make them as efficient as possible. DLVO-theory based polyelectrolyte multilayering (PEM) is used for modification of charged fiber surface.

PEM aim for increased interfiber bonding. The time dependant adsorption is based on the opposite charge of anionic fibers and electrolytes and fundamentally in minimizing the Gibbs energy (Fleer et al., 1993; Taipale et al., 2010). It is a question of charge balance of the furnace. (Roberts, 1996) Since the polyelectrolytes are excessively adsorbed onto fiber surface (van de Steeg et al., 1992), a secondary layer of anionic strength polymer can be adsorbed to the cationic layer (Pettersson et al., 2006[a;]). This technique enables the use of combinations of more cost efficient natural polymers.

The surface forces have great effect on assuring the stability of colloidal system. The interaction of charged surfaces follows the Derjaguin- Landau- Verwey-Overbeek theory (the DLVO-theory) illustrated in the *figure 15.* At certain distance the electrostatic repulsion is dominant. To get the electrical double layers cross, polyelectrolytes must get in close contact with the particles, this is achieved by e.g.fluid or Brownian motion. VdW forces and electrostatic double layer together form the net sum of interaction between two surfaces. (Eronen, 2011)

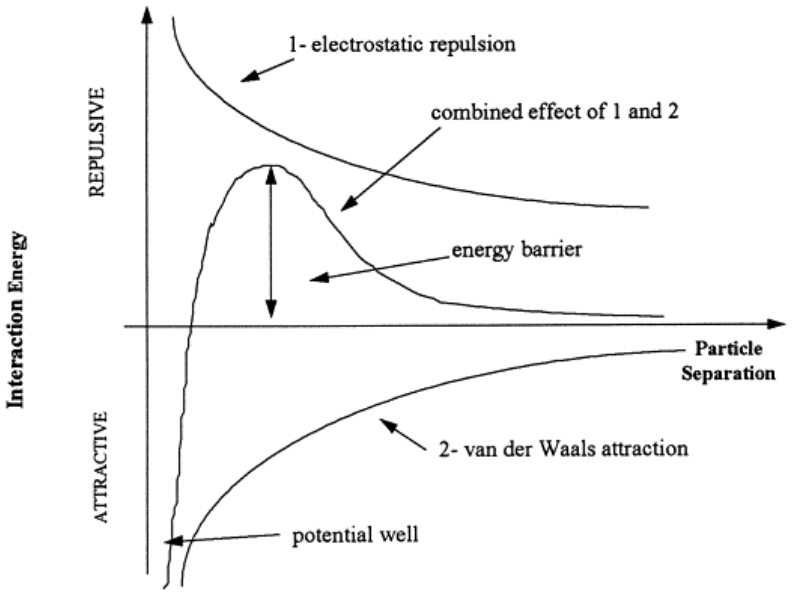

Figure 15. Representation of DLVO theory (Thomas et al., 1999)

The overlap of the double layer is referred as the Debye length and is dependent solely on ionic strength (Eronen, 2011) When Debye length decreases, the attractive vdW forces come in place. The electrical interactions are dependent on the thickness of the electrical double layer in the manner that the distance between two surfaces needs to be smaller than twice the double layer thickness. (Tadros, 2015) The magnitude of counterions increase near oppositely charged particle surface. The increase in ionic strength in the diffuse layer causes a compression of electrical double layer leading to flocculation. (Eronen, 2011; Österlund, 2017) as illustrated in *figure 16.*

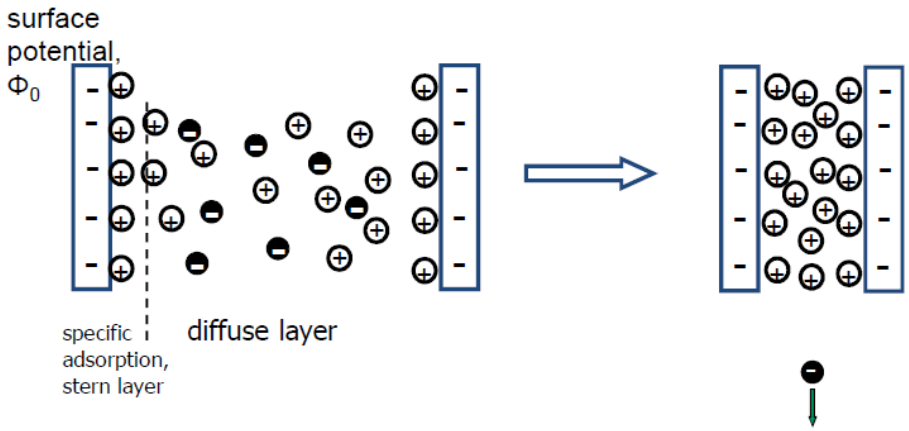

Figure 16. Illustration of particle interaction (Österlund, 2017)

The magnitude of adsorption can be affected with salt addition to certain limit. E.g. increase of Sodium chloride (NaCl) in the medium increases adsorption by

compressing the electrical double layer but eventually excess of it will decrease the adsorption (Wågberg, 2000); Tadros.2015) Greater electrolyte concentration has positive effect on adsorption. The increase in volume fraction of particle decreases the Debye length. Shorter Debye length results in decreased repulsion and increased adsorption. (Tarros, 2015) Then again, higher molar mass of the electrolyte does not guarantee better adsorption. (Pettersson, 2006b). Adsorption can also be affected through refining. Increased surface area induces more -OH -bonding sites and hence, increases adsorption (Pettersson, 2006b.

When the electrolyte has initially adsorbed to the surface, it starts to reconform on the surface as illustrated in the *figure 17*. In addition to concentration, molecular weight and charge density, also pH has effect on adsorption and to be precise, to the conformation of the electrolyte.

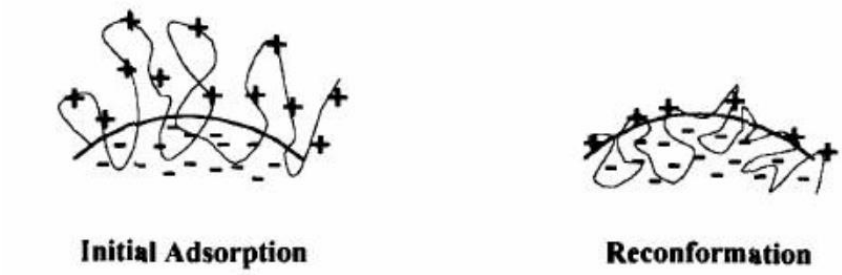

Figure 17. Polyelectrolyte chains start to reconform after initial adsorption (Thomas et al. 1999)

Increased pH decreases the charge of the polymers, which gives the polymers more extended conformation. In turn, highly charged polymers in low pH medium have flat conformation. (Notley & Norgren, 2006) The following subchapters presents shortly the essential elements, which contribute to the adsorption.

3.2.1 van der Waals forces

The interaction between particles is based on the intermolecular repulsion and attraction. Attraction can be thought as the work needed to overcome repulsion. (Tadros, 2015) vdW forces are always present, they can be repulsive or attractive, but always attractive between similar particles (Eronen, 2011). The interaction of the molecules depends on the polarity and polarizability of particles and media. (Österberg, 2017) vdW forces are found between following interactions (Tadros, 2015):

- dipole dipole (Keesom)

- dipole -induced dipole (Debye)
- London (dispersion)

-The Keesom forces occurs when polar permanent dipoles are considered. The attraction is between two molecules with permanent dipoles. The magnitude of the force is dependent on the electronegativity difference between two molecules. This interaction is also found to be temperature dependant, since dipoles are not freely rotating.

Debye interaction is a result of polar and nonpolar molecule, it is always attractive. The induced molecules occur when the dipole of the polar molecules polarizes the other molecules and repels its electrons. Debye can occur only between molecules, not atoms

London interactions are always present. They are consequence of electron density fluctuation in an electron cloud. The fluctuation results, that system seeks for lower energy and the temporary dipoles become aligned. (Tadros, 2015; Leite, 2012)
The vdW interaction energy between molecules is dependent on the chemistry and is described by Hamaker constant, which is material-specific (Eronen, 2011). Additionally, the geometry of the system is taken in consideration. The vdW interaction between flat surfaces is presented in equation (3).

$$W = -\frac{A_H}{12\pi D^2}\ , \tag{3}$$

where

W	is	vdW interaction energy
A_H	"	Hamaker constant
D	"	distance between surfaces

and between flat surface and sphere in equation (4):

$$W = -\frac{A_H R}{6D}, \tag{4}$$

where R is the radius of the sphere. (Österlund, 2017)

The previous interactions are valid in vacuum conditions. The role and the effect of medium should also be considered, since colloidal systems in paper making are in aqueous environment. In an electrolyte solution, the presence of ions screens the interaction of permanent dipoles. In this situation Hamaker constant and Lipsitz theory are applied together, this way the drop of the low frequency interaction is ignored. (Tadros, 2015) The Lipsitz theory has additional benefits, since it considers the effect of temperature and refractive index of the media (Österlund, 2017).

3.2.2 Chemical bonds

Ionic bonds are created between electronegative elements and electropositive ions, which greater than 1.7 differences in their electronegativity. A good example of these electron sharing molecules is NaCl. Covalent bonds have electronegativity difference smaller than 1.0. Compounds with great difference in electronegativity are called electrolytes, since they create an electric current when dissolved in water. The solvent and pH have effect on the ionization of the electrolyte. Stability in the medium is based on the electrostatic repulsion of electrons and the distance of valence electron pairs. (Biermann, 1996) In cellulosic systems the retention of cationic starches is due to the ionic interaction between acidic groups of cellulose and the cationic group of the starch (Roberts, 1996).

3.3 Synthetic strength chemicals

Paper and board are subjected to strong elongial stress during forming and the matrices must have suitable chemistry. Therefore, different types of high molecular weight chemicals are added to the pulp during pulp making process and during paper forming to activate and increase the interfiber bonding. (Vainio & Paulapuro, 2007) The retention of these chemicals is very essential. The chemicals must be adsorbed to the surface of anionic fibers very efficiently, otherwise there will be no additional strength effect. Additives are usually natural or synthetic origins starches and vegetable gums or water-soluble resins, such as polymers of acrylamide. (Roberts, 1996)

Polyacryle amide (PAM)

PAMs are multipurpose polymers, functioning in wide pH range. They are additionally used as drainage and retention aids. *Figure 18* illustrates the basic structure of polyacrylamide block.

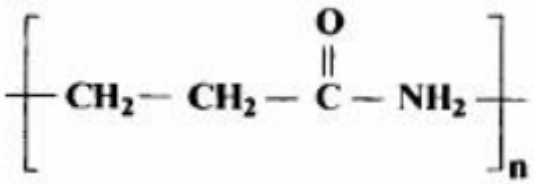

Figure 18. Basic structure of polyacrylamide (PAM) (Roberts, 1996)

Polyacrylamide resins can be anionic, cationic or amphoteric by nature. The latter one has both cationic and amphoteric reactive groups. Most commonly used in paper making is cationic PAM. It is manufactured by introducing tertiary or quaternary amino groups into the polymer. (Roberts, 1996) Use of anionic PAM needs addition of cationic component, since the fiber surface is anionic. The Anionic PAM can also be copolymerized with cationic group directly to the backbone of the polymer. (Holik, 2006) Polyacrylamides are manufactured in large variety of molecular masses. The typical range for dry strength is between 100 000 and 500 000 daltons, and up to 20 000 000 000 (Hietaniemi, 2018) when used as retention aid. To ensure enough bonding sites and secure proper adsorption, the PAM needs to have relatively high molar mass. The efficiency of PAM's is due to short-bridging between surfaces. (Roberts, 1996)

Polyvinylamine resins

PNVF (poly-N-vinylformamide) and PVAm are water soluble polymers. PVAms are chain-type primary amino groups containing polymers, which are available in large variety of molar masses and charge density. These amino groups form bonds with hydrogens from cellulose and increase strength. PNVF as nonionic polymer, has poorer effect on strength than PVAm, which has cationic charge. Relatively low addition of these polymers increases strength without any negative impact on bulk. Economic benefits can be greater if combinations of polymers with different charges and molecular weights are combined. These polymers have more positive effect on strength than refining alone. Polyvinylamine is produced by hydrolysing the polymerized N-vinylformamide. Hydrolysis can be made to desired charge density. (Holik, 2006)

3.4 Spray starch

Starch is the most common used polymer in paper making. It is used to increase both wet and dry strength of paper and board. It can be added to the product in multiple

stages during papermaking. The starch added to the pulp is usually cationic, since the anionic starches are known to have reasonably poor retention. Cationic starch on the other hand has almost 100 % retention. In addition, the starch added to pulp has effect on the dry strength of the product. Spraying in the forming section and surface sizing increase dry strength properties of paper and board. (Roberts, 1996) In spray applications the amount of added starch is commonly between 2- 4 %, which improves dry strength 10-25 % (Maurer, 2009).

Starch is sprayed as uncooked slurry, dispersed in the water. The most important is, that the choice of starch should have as low gelatinization temperature as possible. The gelatinization temperature differs slightly according to the origin of the starch. This is due to the differences is composition and the morphology of the granules. (Mandala, 2012) When cooked starch is sprayed to the top of the wet web in penetrates the fiber mat due to vacuum and increases the strength. of board. The difference with uncooked native starch is that, the granules are sprayed between layers and they gelatinize under drying conditions producing the additional strength at that point. The gelatinization follows the same steps as cooked starch. The granules start to swell in the water containing environment. and gelatinize in product specific temperature, between 50-72 °C (Ruy &Lee, 2007). This is followed by pasting, gelling and in some extent retrogradation. Retrogradation might not be an issue in this application, since the cooking and drying are done simultaneously.

The improvement of strength is dependant on the retention of starch between plies and success of gelatinization. When granules are considered, there is a joint effect between concentration and drying temperature. Ruy &Lee (2017) found that uncooked granules act like fillers. Increased temperature up to 80 degrees Celsius increased plybond strength, but if concentration was simultaneously increased, it affected negatively on the strength properties. (Ruy &Lee 2017) In short, the requirements for successful spraying are suitable amount of moisture, temperature exceeding gelatinizing point including long enough drying time. Since the board needs to reach high temperature, and uncooked starch granules have negative effect on strength, the application is not suitable for fast machines. (Ching, 2016)

4 AQUALAYER TECHNOLOGY

Formation of layered multiply boards is a demanding process involving large number of challenges. One of those, perhaps the greatest, is the mixing of stock layers after headbox. This is conventionally controlled by mechanical elements, by adjusting and controlling the turbulence. Nevertheless, some mixing is always present. This has a deteriorating effect on the board quality. The negative impact has increasingly greater meaning, since the consumption of low quality recycled fibers is still vastly growing. (Cecchini et al., 2016)

For a while, it has been acknowledged that a barrier between the stock layers would be a possible solution. Egelhof (1983) presented an idea of water barrier between the layers and even suggested possibility for delivery of fines in the water stream (Egelhof, 1983). Söderberg (2005) saw possibilities with the application and filed a revised solution of the application. He recognized that the previous invention demanded accurate positioning of elements and was due to cause unwanted mixing of the layers. He also noted, that with previous application different volume flows were impossible to implement, not forgetting that the speed of the flow had to be fixed. Instead of having a flow duct extending from the inlet end to the center of the headbox with rigid partitioning walls, he proposed a model with freely movable blade device. The idea of mobility was to minimize possible pressure differences. For the water barrier delivery, he suggested two approaches. The first one had water pumped through bladed in internal channels. The second proposal involved water flow thru a screen. The core meaning of two approaches was to minimize or delete pressure differences and fluctuation in water flow rate. (Söderberg, 2005)
A recent solution for the water barrier is so called “Aqualayer”. It also consists of traditional mechanical lamellas and use of water as barrier between the stock layers. *Figure 19* illustrates the invention, in which, a thin water layer is fed to the headbox.

Figure 19. Illustration of aqualayering (Valmet, 2018)

The water used is white water from the downstream of the papermaking process. The water is fed from the storage means to the head box via pipes. Mechanical elements depending on the headbox choice are implemented to assure disturbance free jet flow through the slice exit. *Figure 20* illustrates difference of the layer purity between traditional (on the right) and novel aqualayer (on the left) application.

Figure 20. A high-speed camera image of board exiting the slice with aqualayer (left) and without aqualayer (right). In the left picture the water barrier is the white stripe between colored pulp layers. (Cecchini et al., 2016)

The high speeed image clearly demonstrates the existens of the water layer resulting in excellent layer purity.

Aqualayer application does not only provide better formation, it comes with additional benefits. The method allows to use the water layer as a carrier for additives, such as cationic starch or even fiber fractions. This allows to increase the plybond strength by introducing the additives at the latest possible spot. Especially when cationic starch

is considered, the advantage of introducing it in such late phase has obvious advantages. As illustrated in the *figure 21,* due to long contact time, the conventional (a) wet end based cationic starch addition allows adsorption and reconformation of starch on the fiber surface before the web is fully developed. The short contact time (b) promotes stronger flocculation by preaggregation of fines from the white water. By adding additional chemicals,

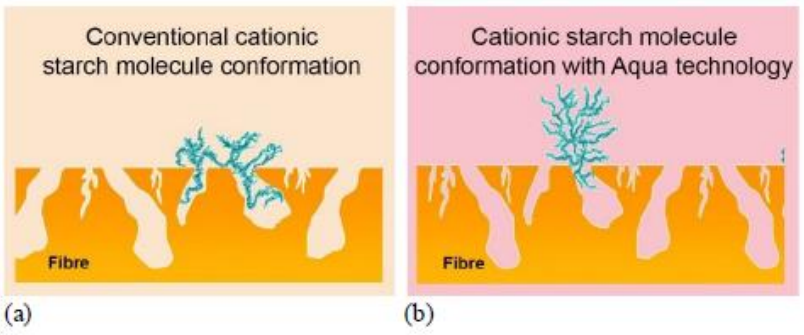

Figure 21. Differences in conformation with long (a) contact time and short (b) contact time (Cecchini et al., 2016)

the retention of starch can be improved, and hence reductions in costs can be achieved. (Cecchini et al., 2016) Since this application introduces a possibility for additional parameter, the water layer has opened a whole new window for strength improvement studies. The attempt to increase the quality of recycled material has been approached with refining and fractionation. It has been found, that suitable size refined fines fed in the water layer promote strength, since refining reactivates the fibers and increases relative bonding area. By these means the starch content can decreased, and simultaneously achieve increased strength even with higher filler content. (Cecchini, et al., 2016; Cecchini & Turpeinen, 2016)

5 SPRAY APPLICATION

Spraying has previously been used as coating technology for several paper grades. It also has a role in many other applications related to papermaking. Spray technology is used in large variety of operations from air and dust control to moisturizing during converting (Markets &applications, 2018). Through these, the overall understanding of rheological behavior of sprayed starch and other paper making additives has been studied and developed.

Spraying is a concept were very thin layers of substances can be applied accurately on the surface. Strength improvement can be achieved by spraying either polysaccharides, synthetic strength polymers or combination of those on top of the wet web or between plies. (Salminen et al., 2012; Oksanen et al. 2011; Cowman, 2014) Especially polyelectrolyte multilayers (PEM) benefit from spray application. Formation of multilayers is affected by electrolyte concentration and charge density. The absorption of polymers is essential feature. PEMs tend to promote the adhesion of individual fibres. It has been shown, that by spraying to the surface, the polymers do not interfere as much with fines. This way the polymers are adsorbed to the fiber bonding area. (Oksanen et al., 2011; Salminen et al., 2011; Lingström et al., 2005) Next sub chapters introduces spray technology used in board manufacturing and give an overall picture of the rheology of sprayed liquids.

5.1 Spray technology

The core of the spray technology is at the atomization of liquid. The most common atomizing method is air assisted. The liquid is pressurized thru a spray nozzle with certain flow rate, spreading the liquid into micron size droplets at the outlet. *Figure 22* illustrates the formation of spray.

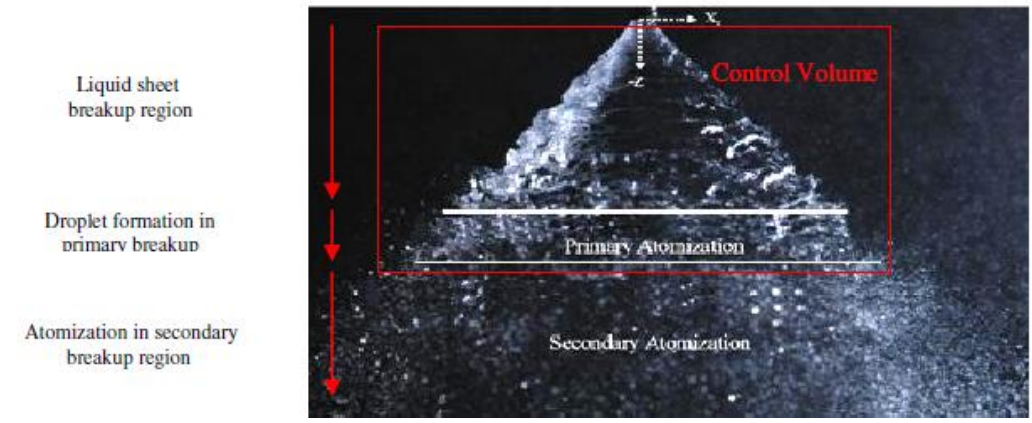

Figure 22. Three steps of atomization of liquid spray (Eberhart et al., 2009)

After exiting the nozzle, the atomization proceeds in three steps. Firstly, the liquid is pushed out in a sheet like form. As the liquid sheet continues moving forward, it starts to break into ligaments at the primary breakup zone. At the secondary breakup zone, the aerodynamic drag becomes equal to the surface tension force (Lefebre, 2017) and the ligaments elongate and break into small droplets (Fernando, 2000) The shape and structure of the ligaments and following droplets are controlled by the geometry of the nozzles. The size and velocity of the droplets are dependent on the viscosity and velocity difference between the air and liquid flow. In other word, smaller droplets have lower velocity. The droplet size is also affected by surface tension and density of the liquid, though, the importance of density is quite meaningless. (Lefebre, 2017) The selection of the nozzle is dependent on the application and its demands. Factors affecting are to the choice of nozzle are (Nozzle-network.co, 2018):

- spray angle and width
- flow rate
- spray pattern
- material manufactured
- pressure.

The alignment of the nozzle bar is in most cases immediately after the head box (Ryu & Lee, 2007; Pulp and paper research, 2013). Penetration of sprayed liquid into the wet web is a consequence of suction of the vacuum pumps (Ryu & Lee, 2007; Steindl, 2014). Nozzles come in variety of shapes and materials. For starch spraying, manufacturers recommend hollow cone or flat nozzle, but it has been proven, that hollow cone nozzle increase misting tendency (Mätäsaho, 2010). At the paper machine the nozzles are fixed in a spray bar, which covers the whole web length. The

nozzles should be angled slightly downwards to avoid misting of starch. (Strong et al., 2006)

5.2 Rheology of sprayed liquid

One cannot emphasize enough the importance of viscosity and flow properties of sprayed liquids. Not only has rheology a great role on the spraying process of the starch solution, but also the combined rheological effect of granular and soluble starch must be considered, as they proceed in different manner in the fiber network.

Firstly, the significance of spray rheology from the spraying perspective is reviewed. The viscosity is the key element, since it controls the flow and hence is the single restricting element of the method. The apparent viscosity of spray starch is usually relatively low, from 50 mPas to 100 mPas (Somerkallio, 2011) but it can be as high as 400 mPas and still be operative (Ching, 2016). Increased viscosity is seen in increased pressure and decreased flowrate. The flow rate of a nozzle is proportional to the square root of pressure Increase in pressure affects increasingly on drop size and drop size distribution, giving poorer surface coverage. (Lefebvre, 2017; Nozzle network.co, 2018) Dynamic pressure, surface tension and viscous forces control the breakage of droplet during atomization (Lefebrve, 2017)

Starch used in spraying has linear viscoelastic behavior. Unmodified starches might experience negative effects such as gel syneresis and breakdown. This might lead to problems in droplet formation. (Mandala, 2012), since Mun et al. (20000) found that high molecular weight solutions experience extensional thickening behavior. (Negri et al., 2013)

Nonionic starches swell less in the water than modified starches. They have lower viscosity; hence higher solids are possible. (Maurer, 2009) When granular starch is sprayed onto wet web before drying, the suction forces caused by vacuum distribute granules evenly into the web. If the web is too wet, the granules migrate excessively, and very small amount is left on the ply surface. In that sense it is reasonable to spray after dry line and prevent unwanted excess migration along with drainage water. (Ruy &Lee, 2007; Mätäsaho, 2010) According to findings of Ruy &Lee (2007), the optimum web dryness for the development of Scott Bond strength is found to be between 8 % and 11 % solids. Most likely the solids are approximately 15 % at the beginning of drainage phase (Lindqvist, 2013)

EXPERIMENTAL PART

In the experimental part materials and methods of folding boxboard study are first presented, followed by testliner part. Then the results of FBB and testliner are separately presented and discussed.

6 MATERIALS AND METHODS

In this chapter the chemicals used, the preparation of the test sheets and paper measurements are presented.

6.1 Chemicals used in the study

Anionic, cationic and amphoteric test products and commercial products where evaluated in the study. Spray starch used was commercial non-ionic food quality corn starch with trade name Maizena. Cationic potato starch Raisamyl 50021 was added in furnish. Commercial FennoPol K3500 P, a medium molecular weight dry cationic polyacrylamide and Fennosil 442 and Fennosil 2180, silica particles were used as retention aid. T*able 2* presents the chemicals used in the both FBB and test liner study.

Table 2. The Labeling and characterization of tested chemicals for FBB and test liner.

	Charge meq/g	Label	FBB	Test liner
Anionic	-0.65	An1 (-0.65 meq/g)	X	
Anionic	-1.40	An2 (-1.4 meq/g)	X	X
Anionic	-1.1	An3 (-1.1 meq/g)	X	
Anionic	-2	An4 (-2 meq/g)	X	X
Anionic	-4	An5 (-4 meq/g)	X	
Cationic	0.78	Cat1 (0.8 meq/g)	X	X
Amphoteric	-0.20	Amph1 (-0.2 meq/g)	X	
Amphoteric	0.20	Amph2 (0.2 meq/g)	X	
Amphoteric	-0.20	Amph3 (-0.2 meq/g)		X
Anionic	-0.55	An6 (-0.55 meq/g)		X
Amphoteric	0.2	Amph4 (0.2 meq/g)		X

6.2 Furnishes and chemical for FBB

FBB furnishes

The CTMP furnish for the middle layer of folding boxboard sheets was a mixture of 80 % CMTP and 20 % broke. Consistency of the stock was aimed at 5 %. In the calculation, the solid contents (SC) of CTMP was estimated to be 86 % and SC of kraft 94 %. Air dray mixture of CTMP and broke were teared into 5 cm x 5 cm pieces and wet disintegrated with Noviprofibre laboratory pulper, using 80 °C tap water for dilution. The mixture was first pulped for 5 minutes with speed 500 rpm. The disintegration was continued for 30 minutes under 1000 rpm mixing. No pre-soaking was done. 300 ppm of GL10 biocide was added to the disintegrated thick stock. Consistency of the thick stock was measured following standard ISO 4119 and 0.6 % thin stock was prepared. Thin stock was adjusted to pH 7 with sulphuric acid (10 w-%) and conductivity was adjusted to 1.5 mS/cm with salt mixture consisting of 70 % calcium acetate, 20 % sodium sulphate and 10 % of sodium bicarbonate (further noted as salt mixture).

For the top and bottom layer, 1630 grams of once dried bleached softwood (pine) and hardwood (birch) were torn to 5 cm x 5 cm pieces and pre-soaked overnight. The consistency of prepared stock was aimed at approximately 4 %. Each kraft pulp was refined using Voith laboratory refiner. Kraft pulps were targeted to SR value 25. The

energy needed to reach the Schopper Riegler (SR) value for pine and birch pulp was 145 kWh/t and 55 kWh/t, respectively. 0.6 % furnish, consisting of 80 % birch and 20 % pine was prepared. The furnish was adjusted to pH 7 with 10 w-% sulphuric acid. Conductivity was adjusted to 1.5 mS/cm with salt mixture. The both furnishes were characterized before pH and conductivity adjustment. The characteristics of the furnishes are presented in the *tables 3* and *4* The methods and devices used in characterization are presented in the *table 5.*

Table 3. Characteristics of CTMP furnish

Middle layer	**CTMP**				
CTMP	80	%	pH		6.9
Broke	20	%	Conductivity	µs	164.3
			Z-potential	mV	-70.3
			charge	µeq/l	27
			Turbidity	NTU	32
			Consistency	g/l	5.7
			Canadian freeness		498
			Ash 525 C°	%	1.2

Table 4. Characteristics of kraft furnish

Top/bottom layer	**Kraft**				
Birch (SR25.5)	80	%	pH		6.2
Pine (SR23)	20	%	conductivity	µs	127.2
			Z-potential	mV	-58
			charge	µeq/l	20
			Turbidity	NTU	2.7
			Consistency	g/l	5.0
			Canadian freeness		542
			Ash 525 C°	%	0.5

Table 5. Methods and devices used in characterization

Analyse	Device	Standard
pH	Knick Portamess 911	
conductivity	Knick Portamess 910	
Z-potential	Mütek SZP 06	
Charge	Mütek PCD 03	
Turbidity	HACH 2100AN IS	ISO 7027
Consistency		ISO 4119
Canadian freeness		ISO 5267-2
Schopper Riegler (SR)		ISO 5267-1
Ash content	Precisa PrepAsh 229	ISO 1762

6.2.1 Forming of FBB sheets

The sheets, illustrated in *figure 23*, were formed using a Techpap dynamic hand sheet former (DSF),

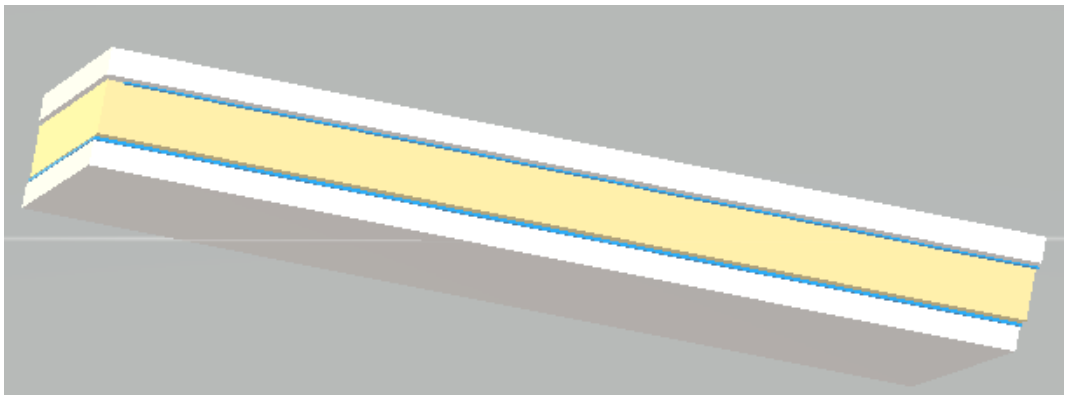

Figure 23. Illustration of FBB three-layer board. Top/bottom kraft. Middle CTMP. Between top/middle and middle/ bottom spray starch.

In principle, as shown in *figure 24*, the core of the machine is a rotating drum mounted on a vertical axis. Inside the drum there is a perforated secondary wall (marked with black arrow). During rotation, water is injected into the drum. Due to centrifugal forces, the rotating water covers the perforated wall and water wall is build up. When forming the sheet, a wire, like one in paper production, is placed on the drum. The furnish is pumped into the rotating drum using a vertical sweeping injector, that does precise and controlled up and down movement. The furnish is delivered to the water wall through injectors spraying nozzle with certain angle. The sprayed fibers migrate

to the wire through the water wall. After spraying water is drained off and paper sheet is formed.

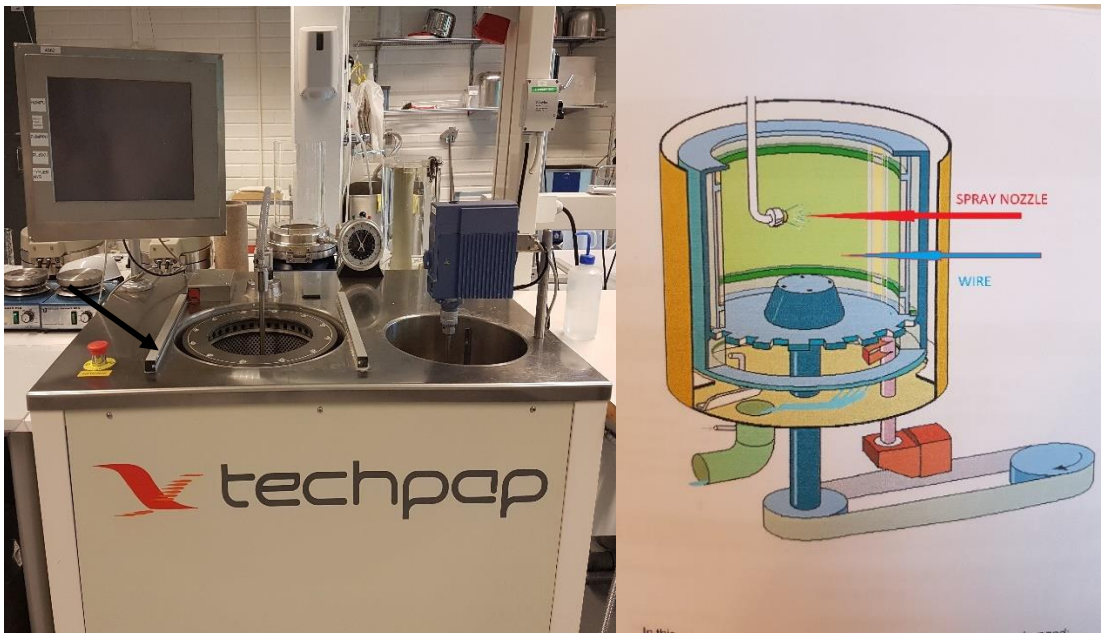

Figure 24. Techpap Dynamic Hand Sheet Former (left) and schematic of DSF drum structure (right)

In this study regular tap water was used as white water, it was adjusted to pH 7 and conductivity 1.5 mS/m. In the study, three-layer multiply boards were formed layer by layer. The total target grammage 225 g/m^2 was adjusted by volume of the pulp in the adjusted tap water. Between layers, a mixture of water, nonionic starch and dry-strength chemicals was sprayed. The amount of water in the spray mixture was two kilograms. The rotation speed of the drum was 1250 rpm, pumping speed 950 rpm/min and the scooping time of drainage was 40 seconds. After water drainage a sample of the wet sheet was taken for solid contents measurement. The sheet was couched to the blotting paper and wet pressed under 8 bars pressure first between two wet felts and blotting paper and second time between blotting paper. A sample for solid contents was taken and the sheet was dried with STFI restrained dryer for 10 minutes in 130 Celsius degrees.

6.3 Furnishes and chemical for testliner

Testliner furnish

A suitable amount of German testliner (RFC)was torn to small pieces and pulped with Noviprofibre, using 80 C° tap water for dilution. Testliner was first pulped for 30 seconds with 500 rpm speed and further disintegrated for 25 minutes and 1000 rpm. Consistency of 3 % was targeted. Small amount of the ~ 3 % stock was further ground with Hollander laboratory grinder, targeting SR value 60 (further noted as SR60 pulp). The 3 % stock was diluted to 0.8 % consistency. The furnish was then characterized and the characteristics are presented in the *table 6*. The furnish was adjusted to pH 7 with sulphuric acid (10 %) and conductivity was set to 3 mS/cm with salt mixture. 300 ppm of GL 10 biocide was added into the stock to prevent microbial activity. SR60 pulp was diluted into a 0.4 consistency.

Table 6. Characteristics of the 0,8 % testliner furnish

Recycled fiber RFC				
pH		8.2	Knick Portamess 911	
Conductivity	µS	183	Knick Portamess 910	
Z-potential	mV	-20.1	Mütek SZP 06	
Charge	µeq/l	66	Mütek PCD 03	
Turbidity	NTU	330	HACH 2100AN IS	ISO 7027
Consistency	g/l	7.8		ISO 4119
Ash 525 C°	%	11.8		ISO 1762

Chemicals used with FBB

Five anionic, one cationic and two amphoteric chemicals were tested for dry strength effect. Commmercial K3500P and silica Fennosil 2180 were used as retention aid. Raisamyl 50021, a cationic potato starch (cationic charge of 0.21 meq/g), was add to the pulp.

6.3.1 Forming of test liner sheets

Two-layer hand sheets illustrated in *figure 25*, were formed with DSF.

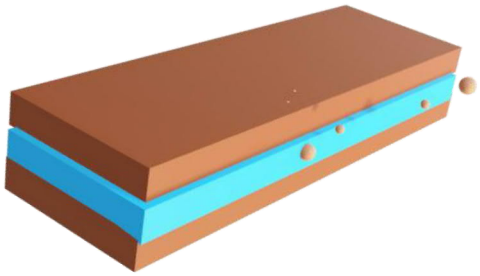

Figure 25. Illustration of Testliner. Aqualayer between top and bottom RFC layers.

Adjusted tap water (pH 7, conductivity 3 mS/cm) was used as white water. An aqualayer, consisting of 1.5 l adjusted tap water, starch, SR60 pulp (3.8 g/l) and strength chemical was sprayed between the layers. The target grammage of the sheet was 100 g/m^2 of which 6 grams was calculated for the aqualayer. The drum speed was 1200 rpm and pumping speed 1000 rpm/min. The drainage speed was set to maximum position of the P2 potentiometer. The sheet was couched to the blotting paper and wet pressed under 4.5 bars pressure first between two wet felts and blotting paper and second time between blotting paper. Sample for solid contents measurement was taken after drainage and after wet press. The sheets were dried using a steam heated drum drier. The temperature of the steam was set to 92 Celsius degrees. The sheets were run through three times, twice accompanied with the blotting paper and third time the sample sheet solely.

6.4 Paper testing

Both FBB and testliner sheets were conditioned overnight according to ISO standard 187, at 50 % relative humidity and 23 °C. Testing of the sheets was done according to table 7. Blistering, microscopy and Scanning Electron Microscope/ Energy Dispersive X-ray Spectroscopy (SEM) are explained separately.

Table 7. Devices and standards used in the testing

Analysis	Device	Standard	FBB	Testliner
Ash content	Precisa PrepAsh 229	ISO 1762	X	X
Basis weight	Mettler Toledo XP2003S	ISO 536	X	X
Blistering	IGT AIC2-5	ISO 3783	X	
Bulk	Lorentzen & Wettre Micrometer	ISO 534	X	X
Burst	Pta Group	ISO 2758		X
Microscopy	MEIJI Techno		X	
Scott Bond	Huygen internal bond tester	T569	X	
SEM	Philips XL 30 Feg FESEM and Oxford Instruments EDS with AZtec software			X
SCT	Lorentzen & Wettre Compression strength tester	ISO 9895		X
Starch retention	Spectrophotomer	T419		X
Viscosity	Brookfield LVT DV-II	KGDMS-182-154		
Z-strenght	Lorentzen& Wettre ZD tensile tester	ISO 1574:2009	X	X

6.4.1 Blistering

Blistering/ delamination of FBB samples were evaluated with IGT dry pick and ISIT passes to fail- test.

IGT dry pick

A known film thickness of IGT mineral based oil of high viscosity was applied to an aluminium printing disk. The oil was applied to the disk with a standard IGT inking unit. The oil was transferred to the sample surface using accelerating speed, where speed increased from 0 m/s to 4 m/s during the application. The point at which the picking and blistering starts is marked and the distance is used in calculations. At a

known oil viscosity, this value relates to the velocity or press speed that can be achieved before the sheet is damaged.

ISIT passes to fail

Figure 26 illustrates the passes to fail is a ISIT test method, where paper strip is fastened to the printing sector (1) The sample is slightly pre-wetted (2) and then printed 10 revolutions with standard sheet-fed off set ink (3). The result is the number of revolutions the sample can go through without delamination.

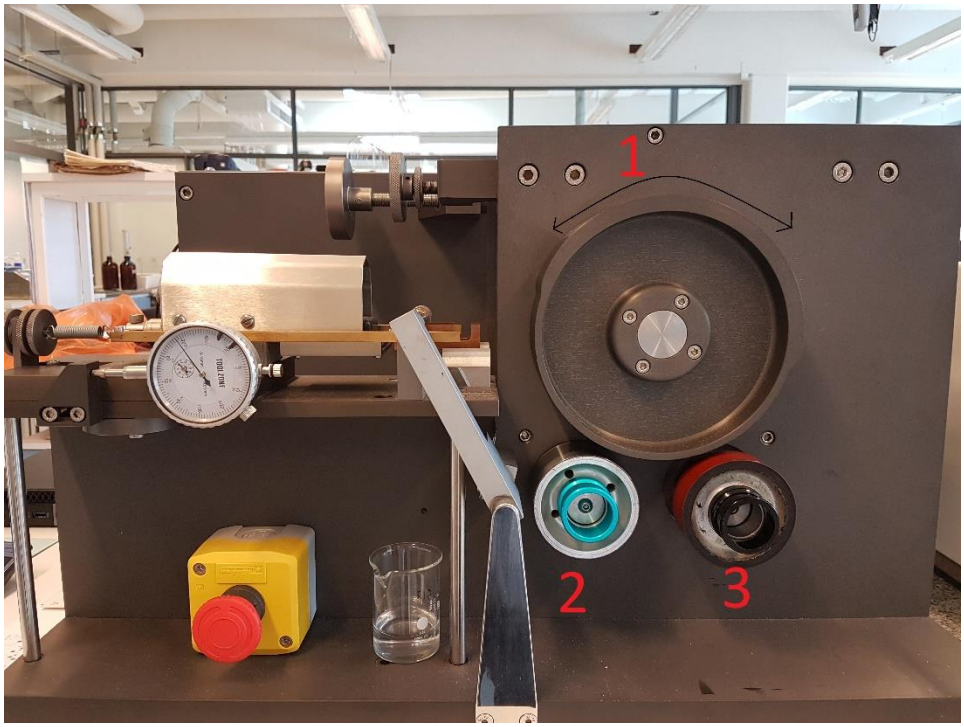

Figure 26. ISIT printing unit. (1) sample sector, (2) water unit, (3) printing unit.

In the test the ink used was Siegwerk Ink, /DIAM 44/ black. The amount of ink applied 1.8 mm³ Printing pressure for moisture unit 400 N, printing unit 300 N and water amount 1.0 g/m². Number of revolution 10 and print speed 2.0 m/s.

6.4.2 Starch retention

Microscopy

The retention and the presence of the spray starch for FBB was evaluated microscopically. A cross-section of the sample was dyed with solution mixture of Iodine (I_2) and Potassium Iodide (KI). The solution was prepared by dissolving 7.5 grams of KI into 10 mill liters of ion- exchanged water. Furthermore, 5 grams of Iodine was dissolved into KI solution. In a solution iodide has a light orange-brown color.

When it is added to starch, a dark blue charge-transfer complex is formed. (Saenger, 1984) The dyed cross-section was photographed for further comparison of trial points.

Spectroscopy

The total retention of starch in FBB was measured rom chosen samples using spectrophotometric method Tappi 419. The method is based on extraction of starch and staining it with iodine.

Scanning Electron Microscope/ Energy Dispersive X-ray Spectroscopy Analysis

The retention of cationic starch was evaluated from testliners with SEM. The SEM/EDS (Scanning Electron Microscope/ Energy Dispersive X-ray Spectroscopy Analysis) is an analytical equipment that can be used to produce an image or determine elemental composition of a sample semi quantitatively by scanning it with a focused beam of electrons. Before imaging the samples were casted in epoxy resin and dry sanded with SiC-paper (grit 120, 500, 1200 ja 2000). On top of the dried sample button, readymade Glugol-solution (KI/I, 0.01N) was added on top. After 60 seconds, excess amount was wiped away and the button was allowed to dry in room temperature and dark environment before analyzing. Glukol-solution stains the starch.

6.5 Viscosity of n-starch/ strength polymer blends

Spray suitability of n-starch and strength polymer blends in 5 % solids content was evaluated by measuring viscosity. Blends with composition 1:3 (strength polymer and starch, respectively) based on dry substance were mixed. Blends were kept under constant stirring on magnetic stirrer. Samples were measured as fast as possible with Brookfield LVT II in small sample adapter according to Kemira instructions.

7 RESULTS OF FOLDING BOXBOARD

In the following part results for FBB strength measurements are discussed. Additionally, starch retention is analyzed by microscopy and spectroscopy. The role of dry contents is also discussed within the preliminary results. During every result section, the preliminary studies are followed by further testing results.
The preliminary tests were carried with 5 kg/t starch addition and dry strength polymer addition levels 0.75 kg/t and 1.5 kg/t levels. Further studies were done based on preliminary results. The interest was to find the most optimized level of strength polymer. The further studies involved cationic starch addition of 10 kg/t and addition levels of 0.4 kg/t; 0.75 kg/t and 1.5 kg/t of dry strength polymer. The addition of spray starch was 3 kg/t through the whole study. The data of the measurements with error limits is presented in the appendices 1 and 2.

7.1 Z-strength preliminary tests

Figure 27 reveals that there is no clear and exact correlation between charge density and Z-strength. The reference sample without spray starch (Ref 0) has greater strength than the first point with spray starch. In the reference the strength is a consequence of water removal, which forces fibers near each other and most likely the cationic starch migrates through the layers increasing the bonded area at the same time. The drop on the strength might be due to anionic nature of native starch. Surprisingly, An1 (-0.65 meq/g) has no effect on Z-directional strength, even on higher dosage level. This can be explained with *figure 31,* which shows that the bottom and middle layer are separated from each other. In this light the sheet formation has failed. It is possible, that the sheet formation has taken too long time, and the chemical has lost activeness, additionally starch has penetrated too deep to the wire side.

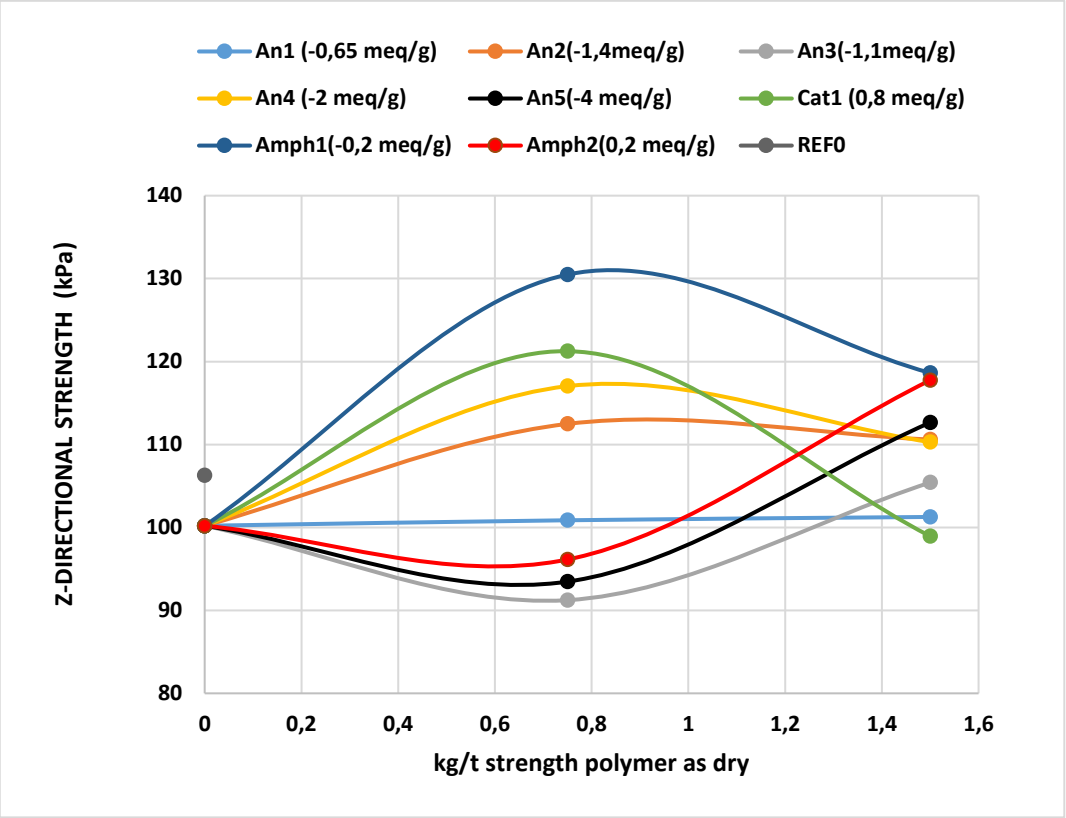

Figure 27. Z-directional strength of preliminary tests of folding boxboard test sheets, with 5 kg/t (dry) cationic starch in top/middle/bottom plies and dosage levels of 0.75 kg/t and 1.5 kg/t of strength polymer as dry between plies, and spray starch 3 kg/t between top and center ply and between center ply and back ply.

Interesting is, that slightly anionic amphoteric polymer has the best response on strength, while the oppositely charged Amph2 (0.2 meq/g) at the same addition level has quite poor effect. Explanation might lie in the amphoteric nature of the chemicals, which allows polymers to form bonds with oneself. Conditions of forming turbulence etc. influence in bonding. An2 (-1.4 meq/g) promotes modest increase on strength reaching plateau already at 0.75 kg/t addition level. Cat1 (0.8 meq/g) and An4 (-2 meq/g) promote moderate strength with 0.75 kg/t, but with higher dosage the strength starts decrease. The spraying method itself promotes mechanically adsorption of chemicals and native starch granules to the fibers even without cationic counterpart in the spray mixture. During testing it was observed that failing of the tested specimen occurred either between top/middle; middle/bottom or both.

The confidence level of the best performing product Amph1 (-0.2 meq/g) is presented in the *Figure 28,* confirming the relevance of the gained result.

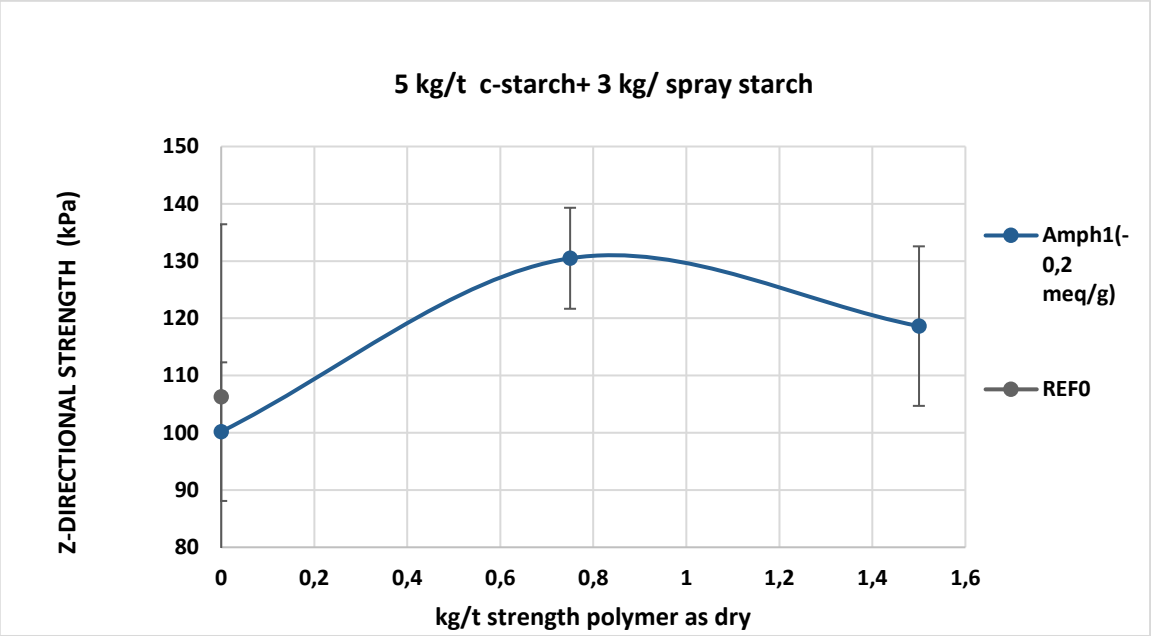

Figure 28. Confidence levels of Amph1 (-0.2 meq/g) Z-directional tensile measurement

The confidence levels of best performing trial points and the reference point are presented in the *table 8*. It can be seen, that the variation in results of reference points is greater when the spray starch is used. With the addition of strength chemicals, the variation decreases, but it is greater with the higher addition level. This might suggest that the cationic starch in the stock has occupied most of the fines surface, and the more chemicals added in the spray, the more there is competition for remaining sites, thus producing more variation inside the measurement group.

Table 8. Confidence level of best performing samples in addition levels 0.75 kg/t and 1.5 kg/t

	95 % confidence level	
REF0	2	
REF1	30.2	
Strength polymer	0.75 kg/t	1.5 kg/t
Am1 (-0,2 meq/g)	8.8	13.9
Am2 (0,2 meq/g)	8.8	13.9
Cat1 (0,8 meq/g)	6.3	12.4
An4 (-2 meq/g)	15.7	9.5

7.1.1 Z- strength additional tests

Chemicals chosen to additional testing, were best performing experimental products.

The starch addition was doubled from preliminary testing. Tests presented in *figure 29* reveal that bringing more cationic starch to the system decreases the performance of anionic Amph1 (-0.2 meq/g). Excess of cationic ions has negative effect on the balance of colloidal system. Already at 0.4 kg/t addition level An1 (-0.65 meq/g) reached plateau level. The maximum addition level for An2 (-1.4 meq /g) was focused and found to be 0.8 kg/t. Additionally, multiplying the amount of starch increased strength by 16 %, likely because the starch was absorbed by several fiber fractions and the bonding area was greatly increased, introducing significantly more bonding sites for anionic polymer. The total strength promoting effect of An2 (-1.4 meq /g) with 0.8 kg/t addition level and 10 kg/t cationic starch was as high as ~36 %.

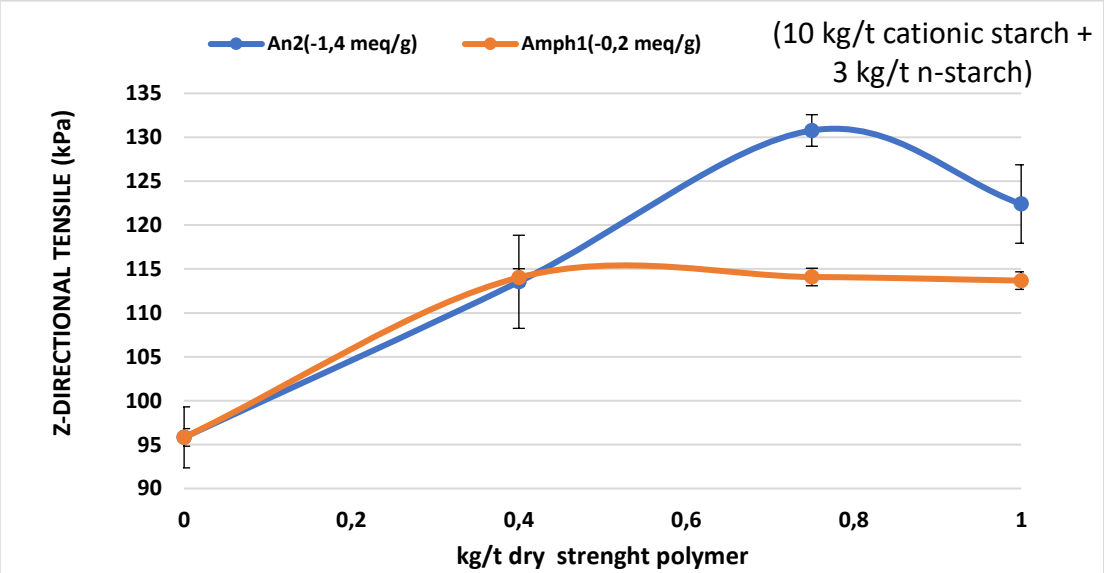

Figure 29. Z-directional strength of additional tests of folding boxboard test sheets, with 10 kg/t (dry) cationic starch in top/middle/bottom plies and dosage levels of 0.75 kg/t and 1.5 kg/t of strength polymer as dry between plies, and spray starch 3 kg/t between top and center ply and between center ply and back ply

7.2 Scott bond

Scott bond was measured from three sample strips. In several attempts the buckle and upper layer of the test specimen was separated from the board middle layer when cutting the tape, due to too low Scott bond of the furnish. It was impossible to get the 15 parallel measurements as planned. Apparently, the cutting blade was slightly damaged. Additionally, there is a possibility that the sheet forming was not a total

success. The unexpected low values and great variation in parallel measurements support this theory. *Figure 32* supports the idea, that some of the sheet have failed. Therefore, the results are not reliable, and they will not be evaluated in this study. However, the results are included in the results appendices 1 and 2.

7.3 Blistering

Samples were first printed with IGT high tack oil, but no delamination or blistering was detected. Because of this, ISIT method was tested, since it provides greatly more viscous ink. This test did not either show indications of delamination or blistering.

7.4 Starch retention

Microscopy from preliminary testing
Microscopy samples were stained with diluted KI/I_2, to explore the location of n-starch granules.

Figure 30 presents the 0-sample without any additional chemicals between layers. The blue arrow beside the 0-sample illustrates the drainage direction, and it applies to all *figures from 30 to 39*.

The starch granules are effortlessly detected between the interfaces. In some samples there are fewer granules present in the top/middle interface, which is an indication that the starch has migrated along the drainage to the wire direction. Also, level of visually observed starch granules varies between wire/middle section of the samples. *Figure 32* reveals, that the An2 (-1.4 meq/g) at 1.5 kg/t addition level has little or non-starch granules between bottom ply and CTMP. *Figure 36* reveals show starch granules have migrated through the plies during water removal.
Nevertheless, it is proven that the granular starch is in some extent fixed between the layers. Based on the microscopy, the effect of strength polymer on spray starch adsorption is not clear.

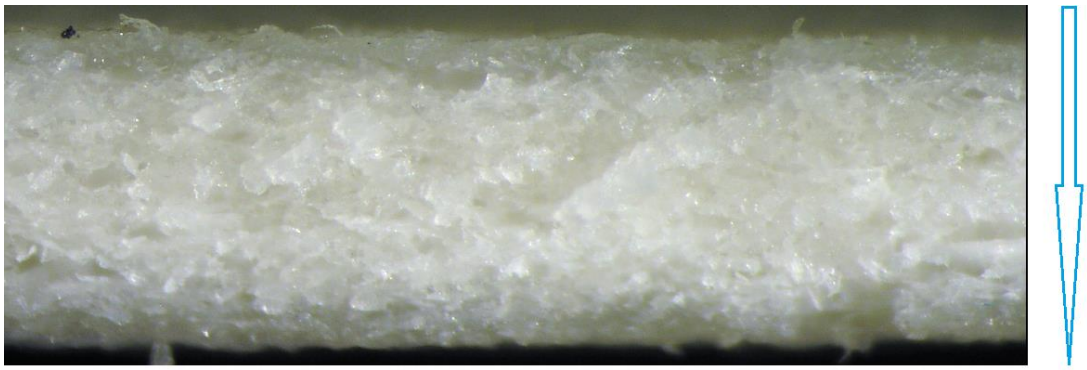

Figure 30. No starch or strength chemicals. The blue arrow beside the figure illustrates the drainage direction.

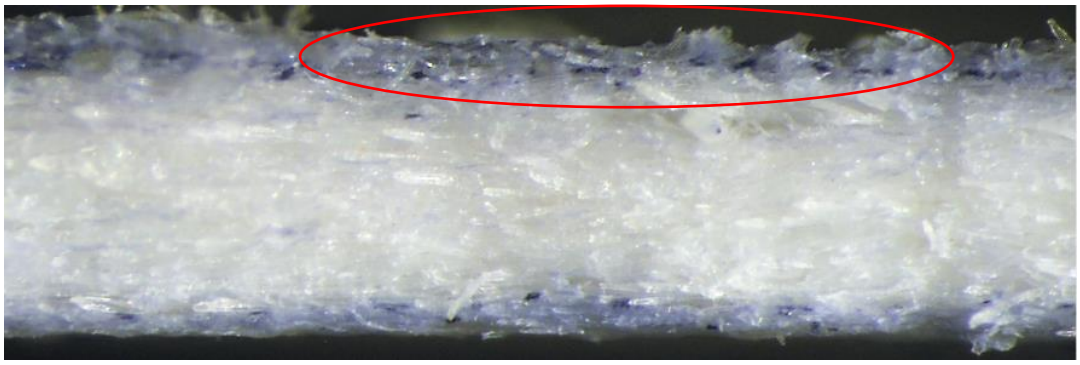

Figure 31. n-starch 3 kg/t as dry between top/middle; wire/middle.

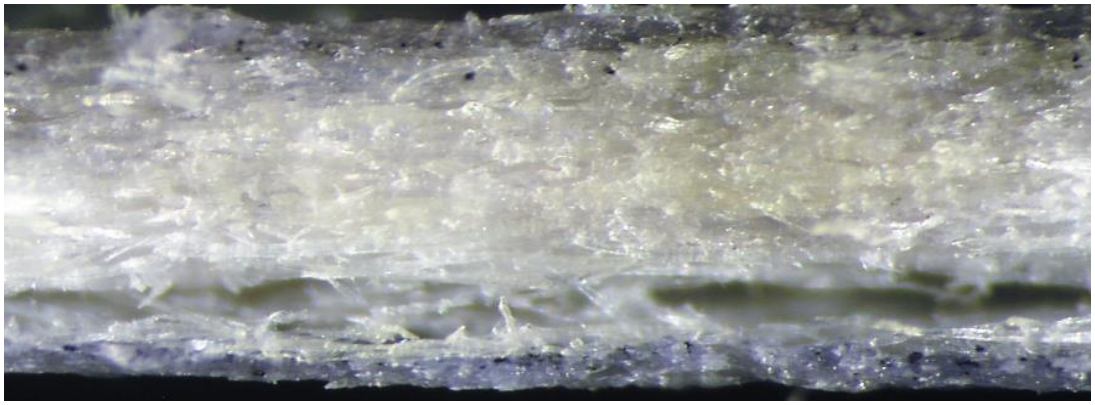

Figure 32. n-starch 3 kg/t +An1 (-0.65 meq/g) 1.5 kg/t as dry, between top/middle; wire/middle.

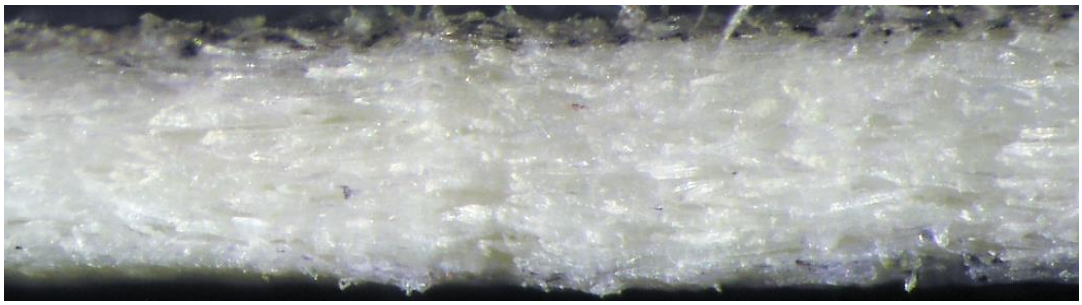

Figure 33. n-starch 3 kg/t + An2 (-1.4 meq/g) 1.5 kg/t as dry, between top/middle; wire/middle.

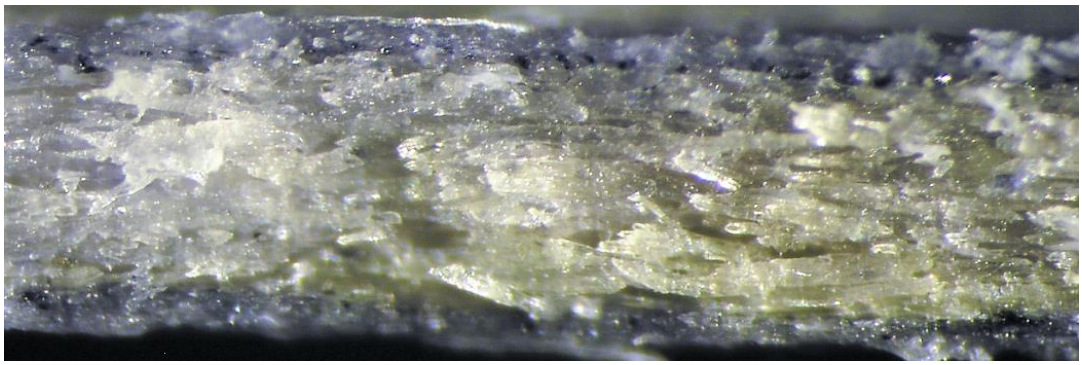

Figure 34. n-starch 3 kg/t + An3 (-1.1 meq/g) 1.5 kg/t as dry, between top/middle; wire/middle.

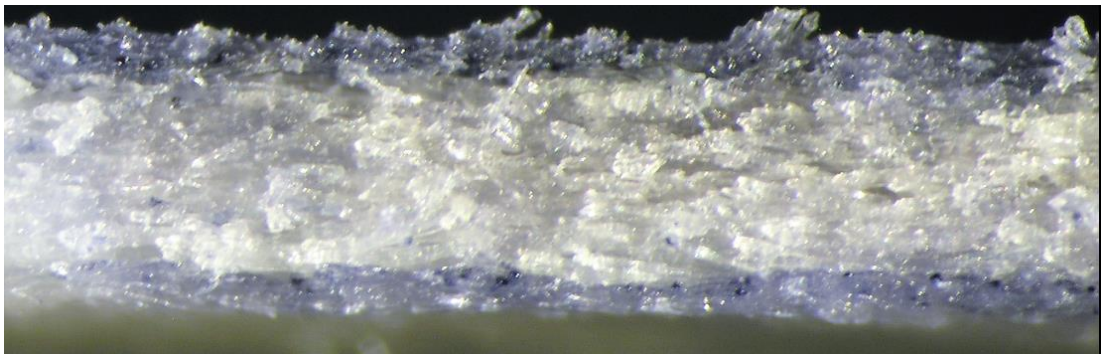

Figure 35. n-starch 3 kg/t +An4 (-2 meq/g) 1.5 kg/t as dry, between top/middle; wire/middle.

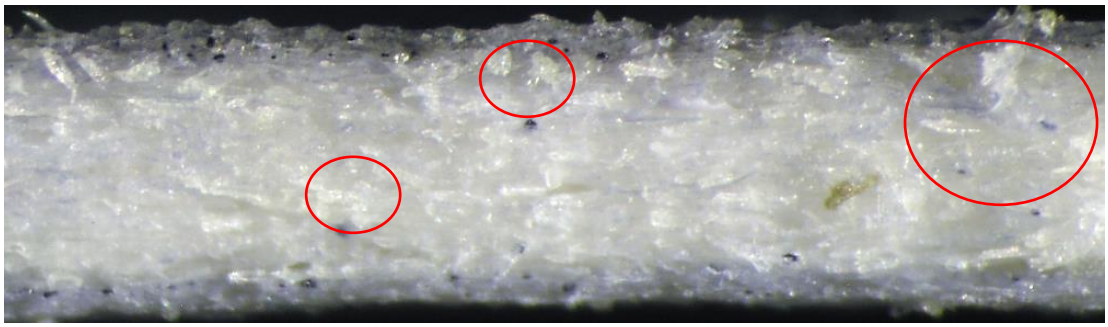

Figure 36. n-starch 3 kg/t + An5 (-4 meq/g) 1.5 kg/t as dry, between top/middle; wire/middle.

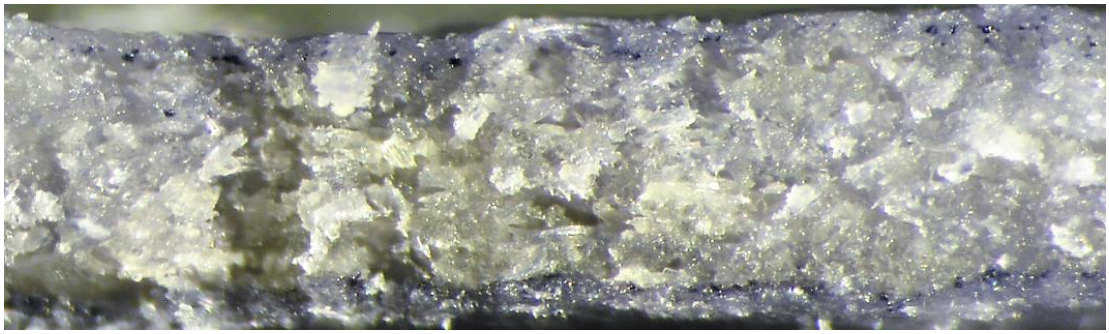

Figure 37. n-starch 3 kg/t+ Cat1 (0.8 meq/g) 1.5 kg/t between top/middle; wire/middle

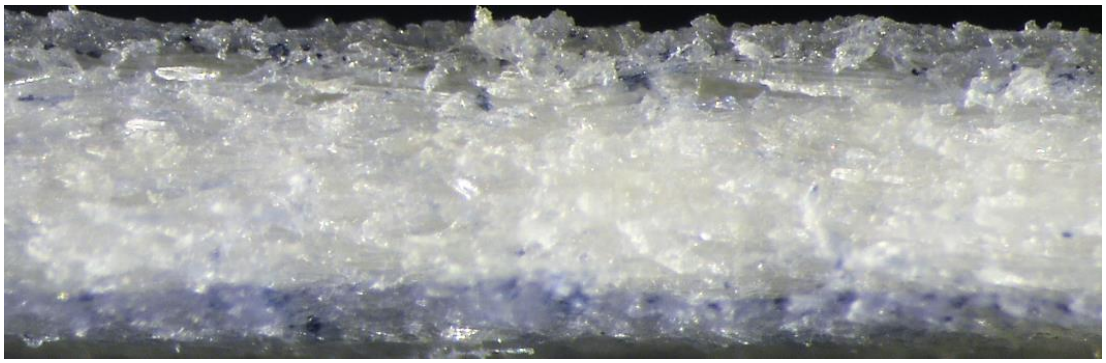

Figure 38. n-starch 3 kg/t+Amph1 (-0.2 meq/g) 1.5 kg/t between top/middle; wire/middle.

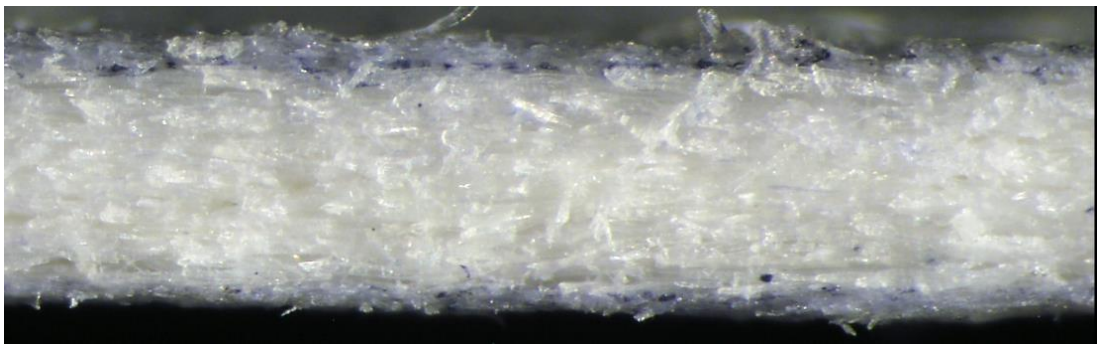

Figure 39. n-starch 3 kg/t+Amph2 (0.2 meq/g) 1.5 kg/t between top/middle; wire/middle.

Spectroscopy

Table 9 presents the measures starch content of selected samples. Calculated total starch amount of the sample is 1.1 %. The reference shows value above that. This might be due to error in sample making. During sample preparations, there were difficulties with vacuum suction when filtering the samples. Apparently, the starch granule is too big for the used filter size, which hindered filtration. This might have consequence, that the extraction with strong acid has been partial. Nevertheless, all

measured values are quite close to the calculated value, which does not seem very likely to be accurate. The total starch retention of cationic starch is usually good. Fibers can absorb starch up to 5 %, but retention of unmodified starch is quite poor (Maurer, 2009).

Table 9. Starch content of FBB samples calculated by absorbance

	Starch %
Ref1	1.3
Cat1 (0.8 meq/g)	1.1
Amph1 (-0.2 meq/g)	1.0
Amph2 (0.2 meq/g)	0.8

7.5 Viscosity of n-starch/ strength polymer blends

Table 10 shows measured viscosities of the spray starch combined with the strength aids used in the study. As mentioned in the literature review, the viscosities cannot be very high, due to limitations of spraying. Current comparison reveals that most of the strength polymers are compatible with native starch. Only An2 (-1.4 meq/g) shows extensive thickening behavior, which makes it unsuitable for spraying. This doesn't mean total rejection of the product, a slight decrease in total solids or addition level can decrease the apparent viscosity to suitable level.

Table 10. Apparent viscosity of n-starch/ strength polymer blends with total solids content of 5 %, out of which 1/3 strength polymer as dry.

	rpm	Spindel no	viscosity (cP)
n-starch	100	18	1.80
An1 (-0.65 meq/g)	100	18	8.2
An2(-1.4 meq/g)	60	31	473.9
An3 (-1.1 meq/g)	100	18	9.7
An4 (-2 meq/g)	100	18	26.2
An5 (-4 meq/g)	100	18	6.3
Cat1(0.8 meq/g)	100	18	41.8
Amph1 (-0.2 meq/g)	100	18	6.9
Amph2 (0.2 meq/g)	100	18	11.5

8 RESULTS OF TESTLINER

Preliminary testing was conducted with anionic, and slightly negative and positive amphoteric strength additives. Burst strength was index to avoid effect of varying grammage. Burst strength is also illustrated as burst kPa values with confidence levels. Also, SCT values were indexed and are presented as geometric mean index of CD and MD measurements, since values differ greatly according to measurement direction.

8.1 Burst

It can be seen from the *figure 40*, that already introduction of refined pulp and starch to the aqualayer increases strength by 13 %. Introduction of An2 (-1.4 meq/g) gives additional 5 % increase to the burst strength at 2 kg/t dosage level. Amphoteric additives have merely negative impact. The sudden drop of An6 (-0.65 meq/g) is also seen in bulk and SCT results. The drop in the results might be due to error in sheet making, since the other two anionic strength additives perform well. The effect of fines is seen in the burst values, but it seems that only anionic chemicals form multilayers with preaggregated fines.

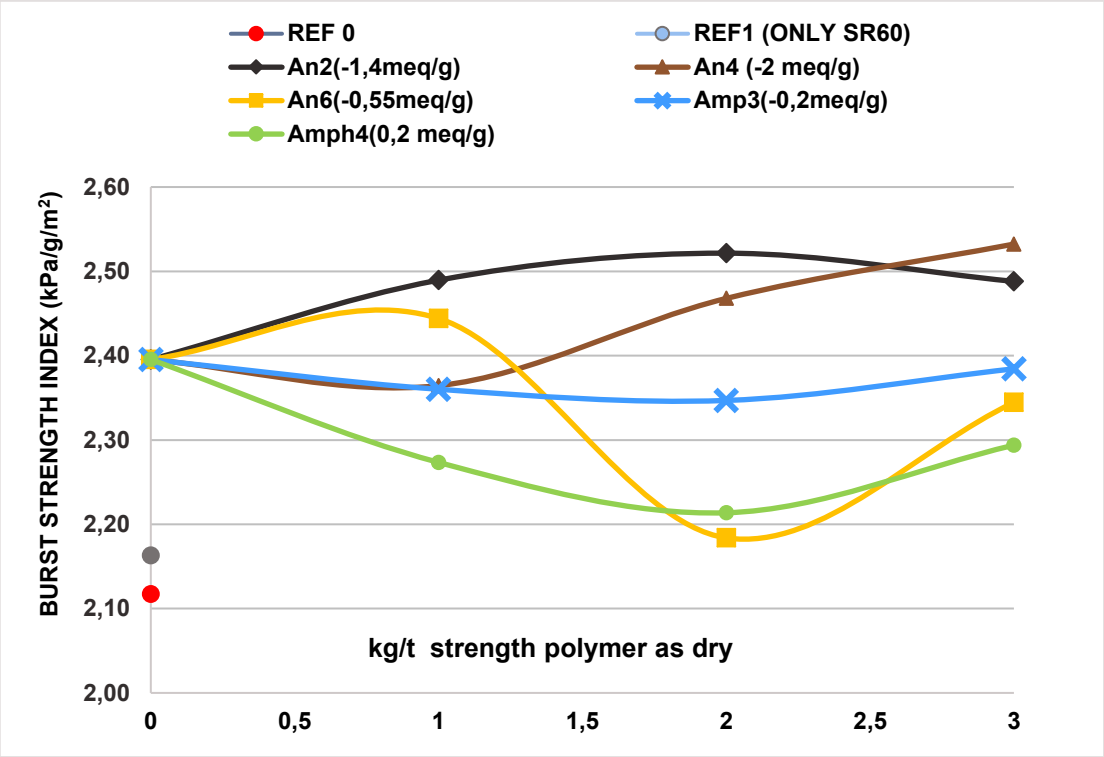

Figure 40. Testliner burst strength index of the preliminary tests. An aqualayer including 15 kg/t (dry) cationic starch, SR60 and dosage levels of 1 kg/t, 2 kg/t and 3 kg/t of strength polymer as dry sprayed between plies

The additional results illustrated in *figure 41* show, that low level of starch with cationic chemical does not promote strength. Cationic starch creates bulky structure, which has decreasing effect on strength properties. The most promising result, index 2.8 kPa/(g/m²) in achieved with 10 kg/t starch and the highest 3 kg/t chemical addition. Nevertheless, nearly the same value (2.75 kPa/(g/m²) is achieved with 15 kg/t starch amount and only 1 kg/t strength chemical level, which makes its more appealing from the economical point of view.

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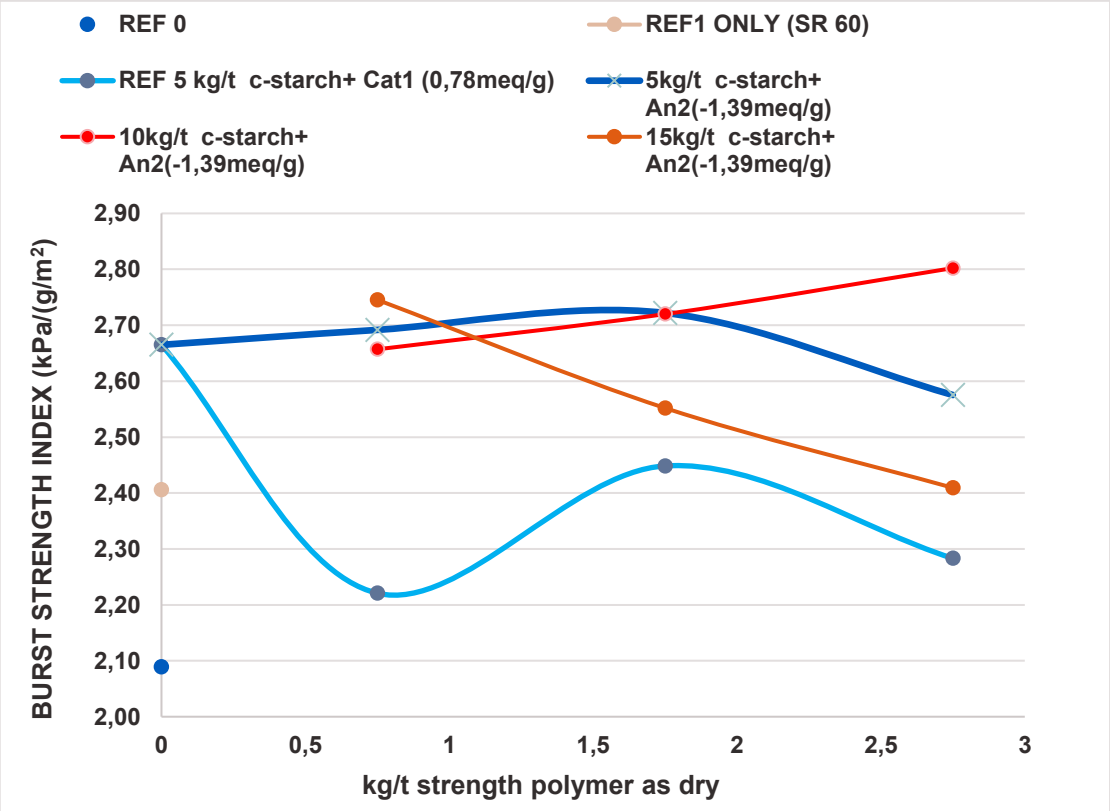

Figure 41. Burst strength index of additional tests of Testliner sheets. Aqualayer between top and back ply was tested with three cationic starch additions levels /5/10/15 kg/t) and strength polymer addition levels 0.75 kg/t, 1.75 kg/t and 2.75 kg/t (dry).

Figure 42 depicts the variation of the measurements. Test points with lower 5 and 10 kg/t starch amount have more significance.

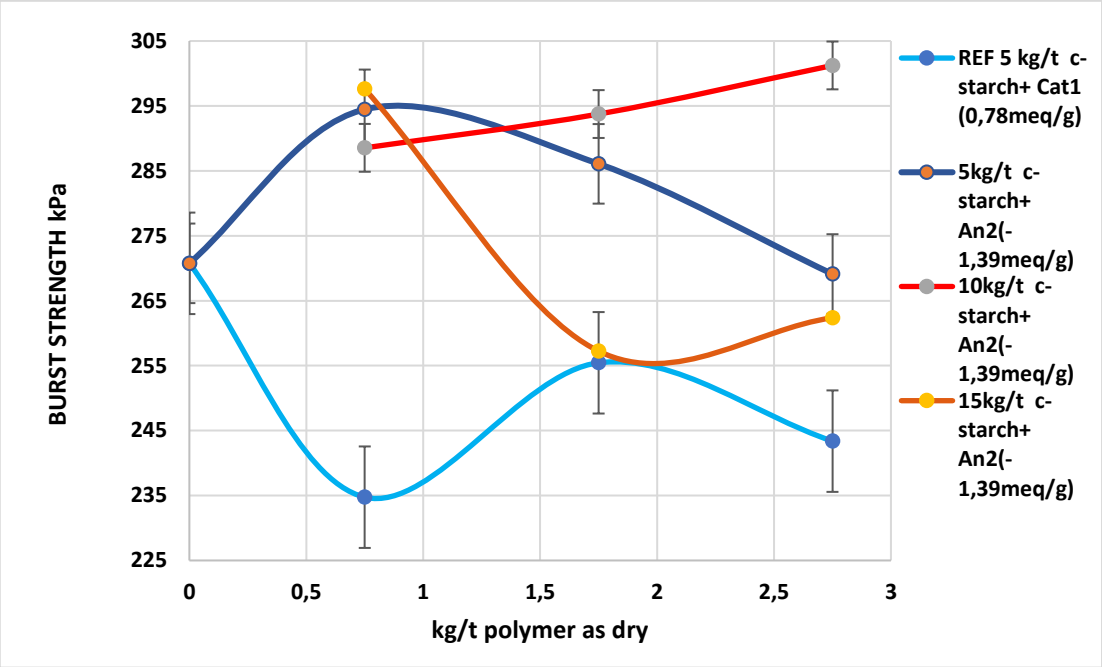

Figure 42. Additional tests of Testliner sheets. Burst strength with error bars. Aqualayer between top and back ply was tested with three cationic starch additions levels /5/10/15 kg/t) and strength polymer addition levels 0.75 kg/t, 1.75 kg/t and 2.75 kg/t (dry).

8.2 SCT (short span compression)

Figure 43 depicts the SCT measurements. Already addition of SR60 has significant effect on SCT. Addition of starch increased strength greatly. Again, only anionic polymers contribute to the ability to resist compression but only on moderate level. Nevertheless, the total contribution to the strength is 18 % compared to the Ref 0 with no additional elements. An2 (-1.4 meq/g) has the greatest positive effect on compression.

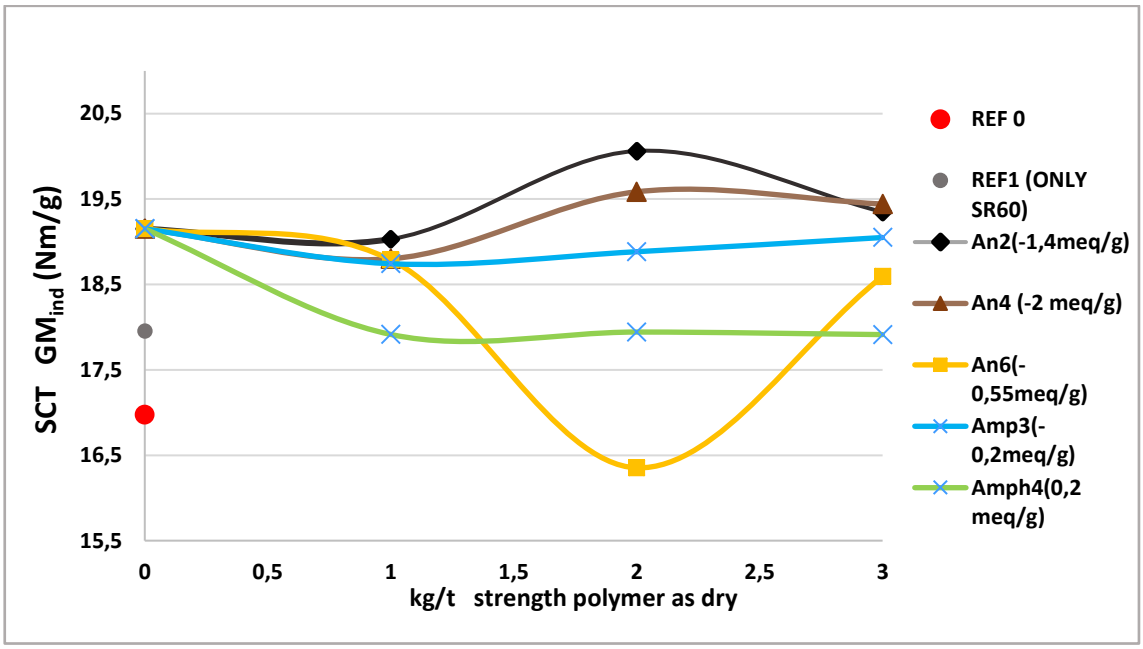

Figure 43. Testliner SCT /GM index of the preliminary tests. An aqualayer including 15 kg/t (dry) cationic starch, SR60 and dosage levels of 1 kg/t, 2 kg/t and 3kg/t of strength polymer as dry sprayed between plies.

Additional tests

Improvement was achieved with SR60 and starch 9.5 %, SR alone 5.5 %, 2.75 parts 19.7 %. Burst correlates with those bulk results, which have moderate standard deviation. *Figure 44* illustrates that cationic chemical has great effect on SCT. It can be that in low starch level the cationic starch occupies the bonding areas of the SR pulp and fines, leaving most of the bonding sites on the wet web for cationic strength chemical. It can also be observed, that amount of 15 kg/t starch stretches for greater addition of strength chemicals thus, increasing the strength value even further.

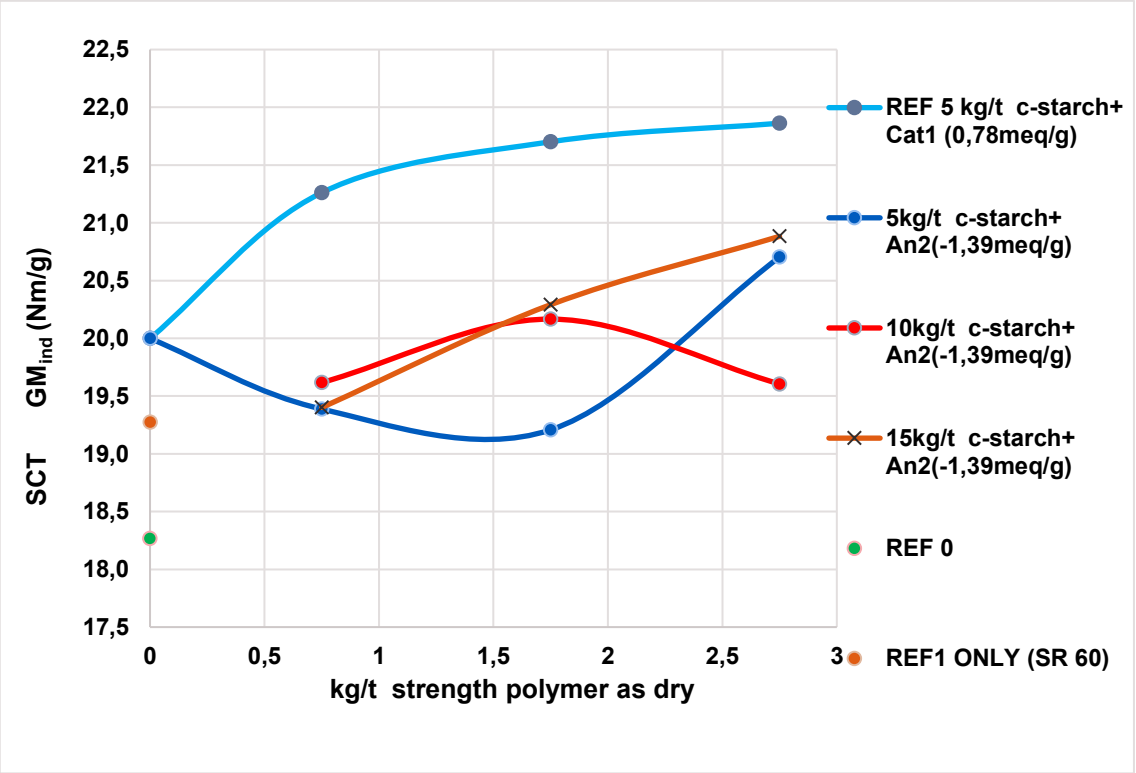

Figure 44. Testliner SCT /GM index of the additional tests. Aqualayer between top and back ply was tested with three cationic starch additions levels /5/10/15 kg/t) and strength polymer addition levels 0.75 kg/t, 1.75 kg/t and 2.75 kg/t (dry).

Figure 45 presents the relationship between SCT GM index and bulk of the additional tests, when starch addition level is increased from 5 kg/t to 15 kg/t. Cationic polymer increases compression strength even with higher bulk values, whereas anionic strength polymer is maintaining bulk constant.

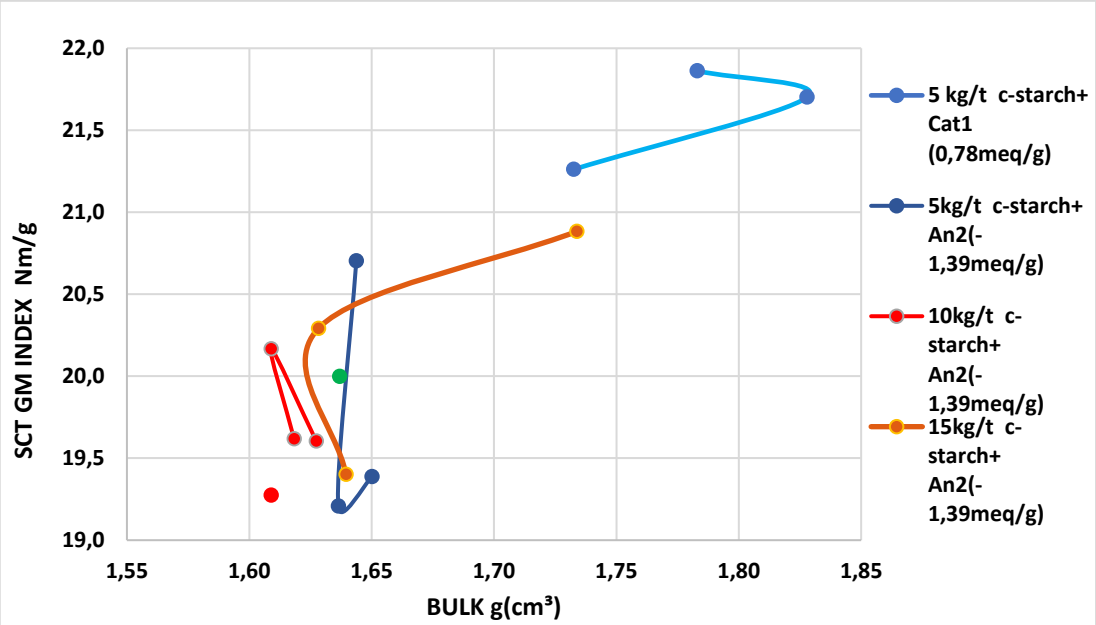

Figure 45. SCT GM index (Nm/g) of additional tests blotted against bulk.

8.3 Z-directional strength

Figure 46 depicts the Z-directional tensile of preliminary testing. Graphics show that SR60 together with cationic starch increase Z-directional tensile 40 % from reference 0 level. The difference between SR60 and SR60+starch is 27 %. Introducing strength chemicals does not give significantly more value to the overall Z-strength. However, it might have effect on the failure position. An2 (-1.4 meq/g) is the only chemical in the study to give some increase on Z-directional tensile.

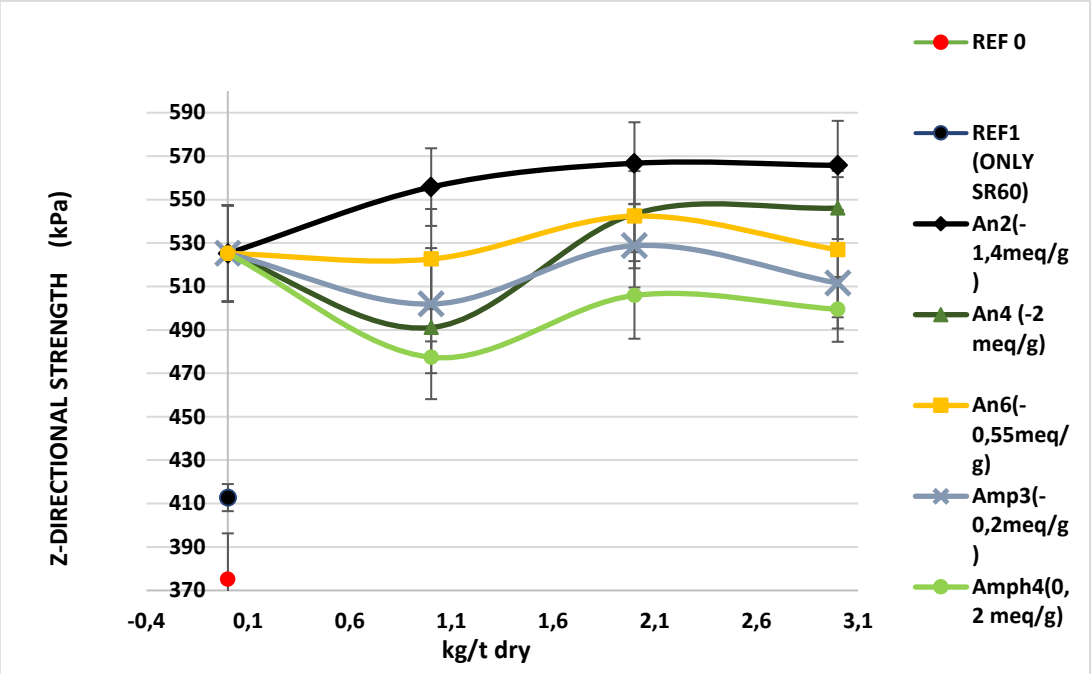

Figure 46. Z-directional strength of the preliminary tests of Testliner sheets. An aqualayer including 15 kg/t (dry) cationic starch, SR60 and dosage levels of 1 kg/t, 2 kg/t and 3 kg/t of strength polymer as dry sprayed between plies.

The Z-strength measurements for additional test points are illustrated in *figure 47*. Graphs show that, increasing amount of starch has strength enhancing influence. Though, the optimum level of strength chemicals varies between different starch addition groups. 15 kg/t starch addition with only 0.75 kg/t An2 (-1.4meq/g) addition gives best performance. Again, this is very positive, since starch is relatively affordable raw material. Overall, strength systems have positive effect of Z-directional strength.

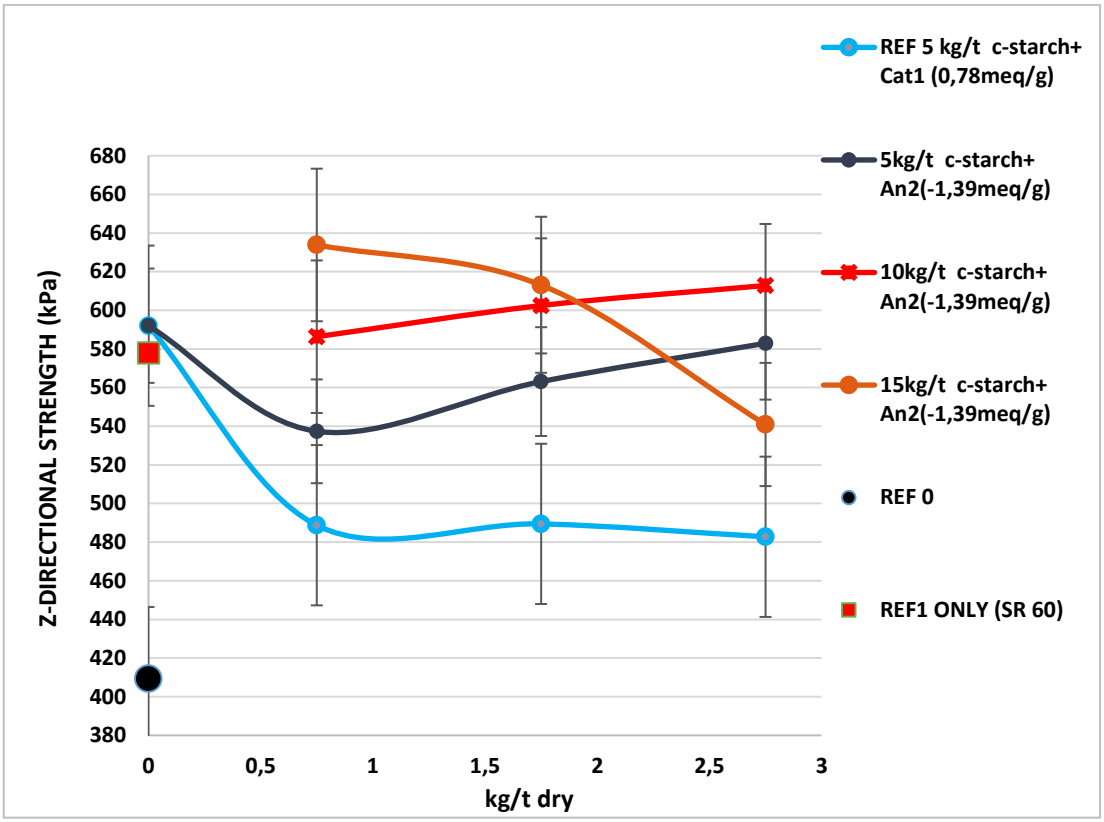

Figure 47. Z-directional strength of additional tests of Testliner sheets. Aqualayer between top and back ply was tested with three cationic starch additions levels /5/10/15 kg/t) and strength polymer addition levels 0.75 kg/t, 1.75 kg/t and 2.75 kg/t (dry).

8.4 Bulk

From the *figures 48* and *49* it can be seen, how bulk dramatically decreases, when additional elements are induced to the pulp. Addition of strength chemicals increases bonding, which is seen in increased sheet density. Typically, increased density has positive effect on SCT. Interesting is, that An2 (-1.4 meq/g) increases bulk when addition level is increased. In CTMP/unbleached systems this type of chemical is known to have decreasing effect on bulk, but with RFC the influence seems to be opposite.

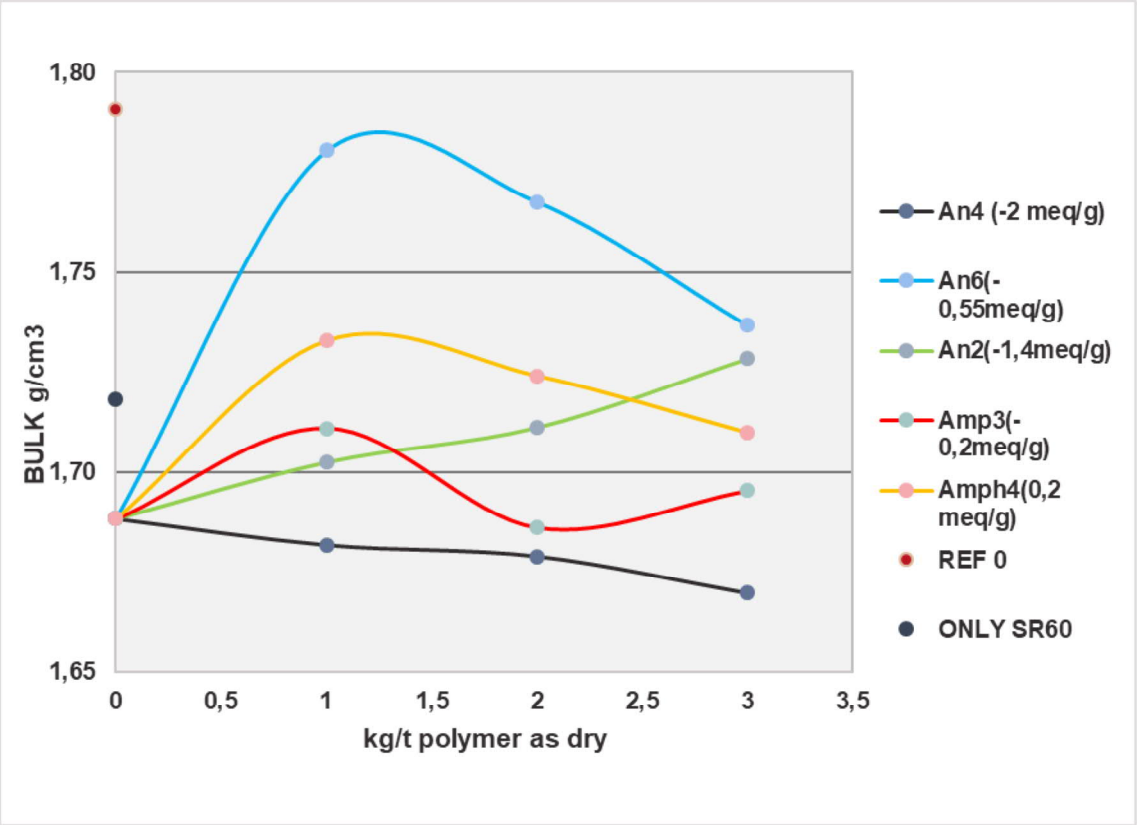

Figure 48. Bulk measured from preliminary tests. An aqualayer including 15 kg/t (dry) cationic starch, SR60 and dosage levels of 1 kg/t, 2 kg/t and 3 kg/t of strength polymer as dry sprayed between plies.

The bulk results in *figure 49 i*ndicate that lower levels of cationic starch with anionic strength polymer results in denser sheets. Whereas, cationic additive has greatly increasing effect on bulk.

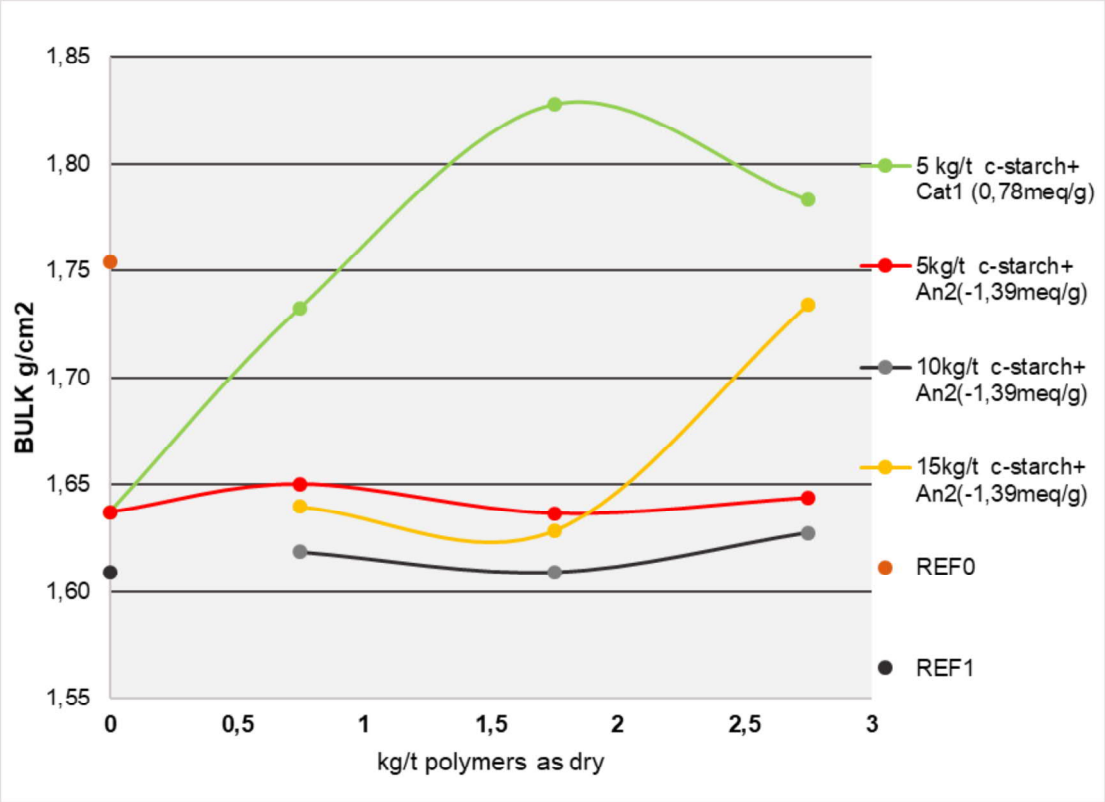

Figure 49. Bulk measured from additional test. Aqualayer between top and back ply was tested with three cationic starch additions levels /5/10/15 kg/t) and strength polymer addition levels 0.75 kg/t, 1.75 kg/t and 2.75 kg/t (dry).

8.5 Starch retention

The Scanning Electron Microscope / Energy Dispersive X-ray Spectroscopy Results

Figures from 50 to 55 present the SEM pictures taken from cross section of the samples. Pictures were taken from samples ref 0 with only water between plies, Ref 1 with 5kg/t starch between plies followed by trial points with had 5 kg/t starch and addition levels of 0.75; 1.75 and 2.75 kg/t strength polymer as dry between plies. In these figures green represents Calcium and purple Iodine stained starch.

Already Ref 0 indicates traces of starch, which is reasonable, since recycled test liner is used. In most of the pictures, larger dyed objects are seen, these are probably larger starch particles. From SEM pictures a layer of starch can be detected in the middle of the cross section. SEM images prove that there is indeed a thin layer between liner plies.

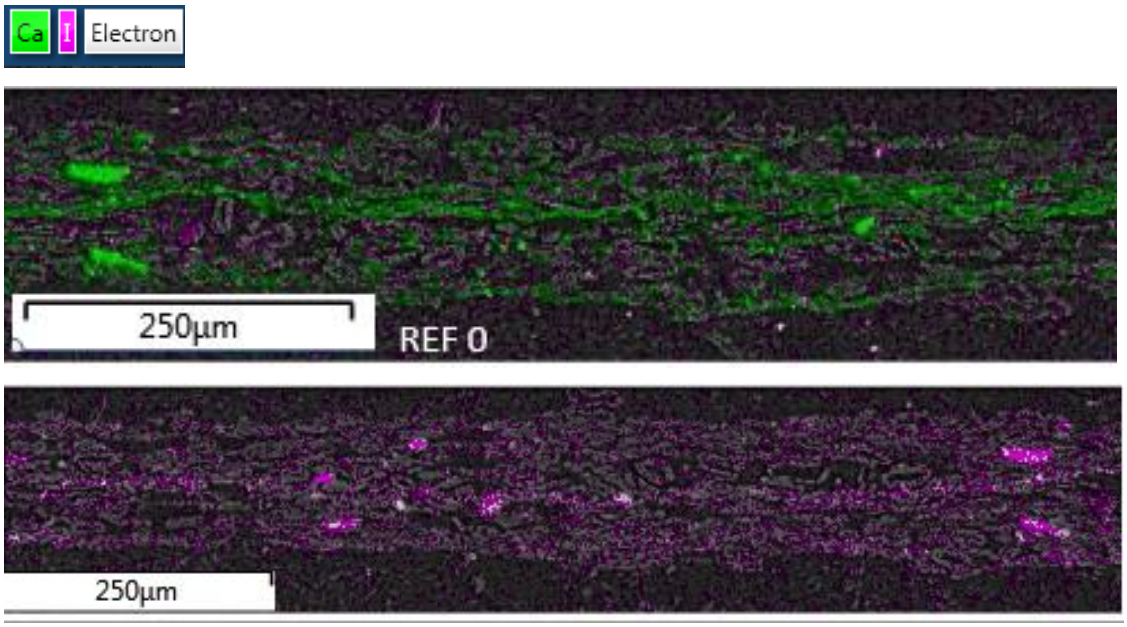

Figure 50. Ref 0, water between plies.

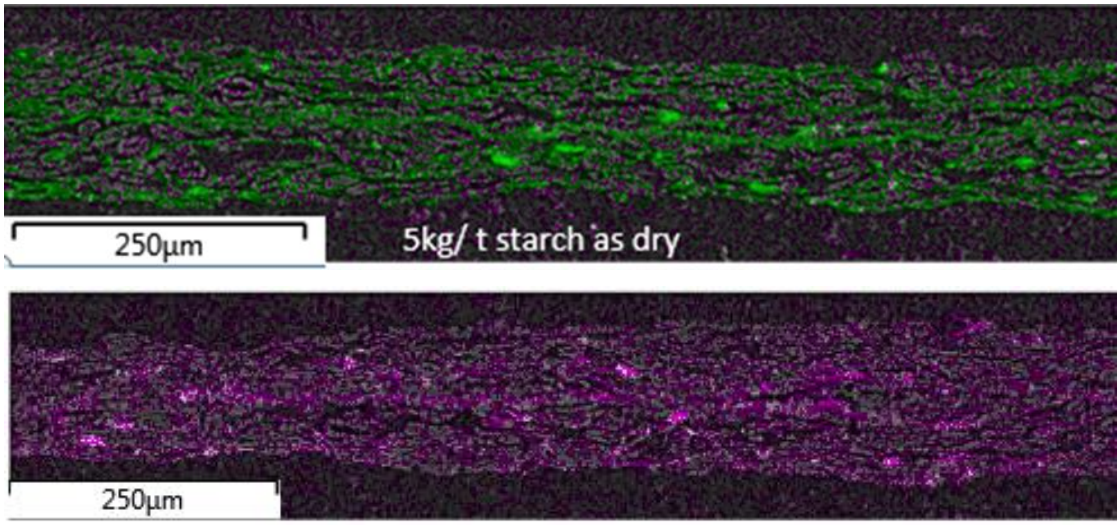

Figure 51. Ref 1; SR60+5 kg/t cationic starch (as dry) between layers

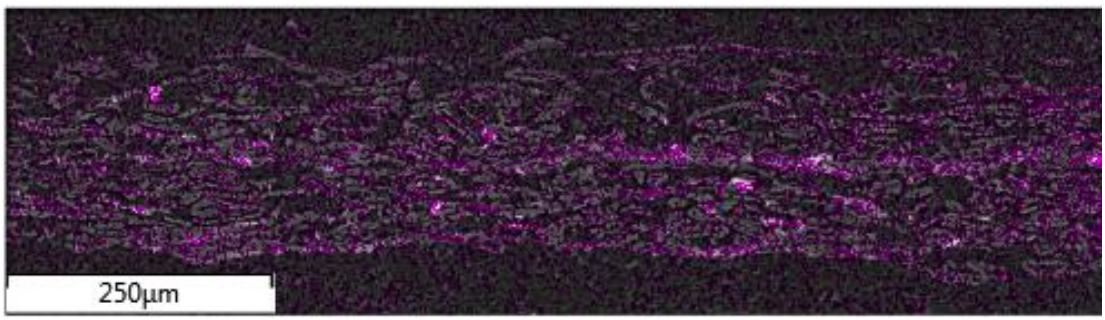

Figure 52. SR60+5 kg/t cationic starch+ Cat1 (0.8 meq/g) 2.75 kg/t.

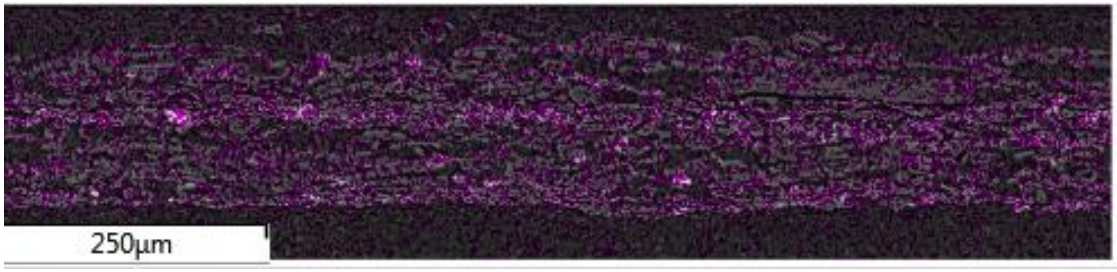

Figure 53. SR60+ 5 kg/t cationic starch+ An2 (-1.4 meq/g) 0.75 kg/t as dry polymer.

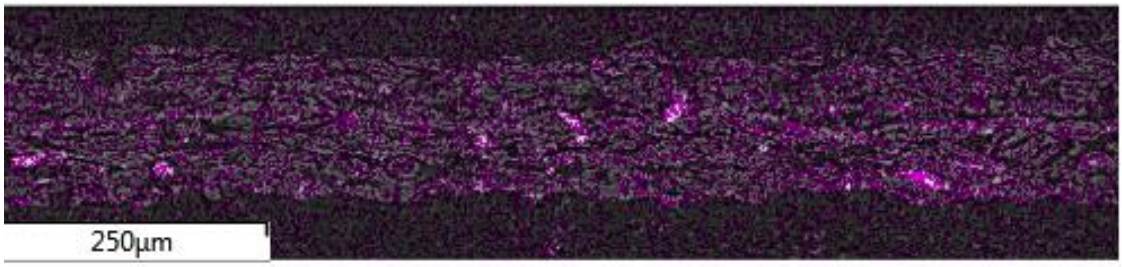

Figure 54. SR60+5 kg/t cationic starch+ An2 (-1.4 meq/g) 1.75 kg/t as dry polymer.

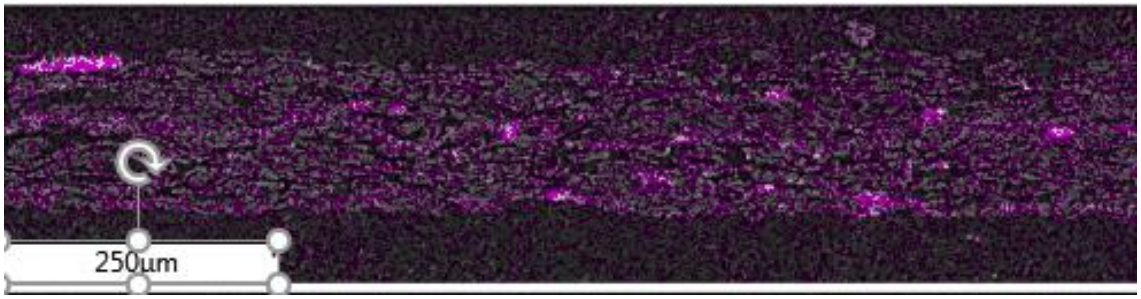

Figure 55. SR60+5 kg/t cationic starch+ An2 (-1.4 meq/g) 2.75 kg/t as dry polymer

SEM also enables semiquantitative analysis of elements, but the values presented in the *table 11* are only slightly directional, since the analyzed portion of the cross section is very small. According to figures the analyzing program has provides, there is no or minor difference between the trial points including reference. Theoretically there should be more starch in the trial points than Ref 0, but that is not the case according to this method. It is very clear, that this is not a proven way to present the amount of starch.

Table 11. A semiquantitative analysis of the composition of the samples.

Element	REF 0	Ref1	Cat1(0,8meq/g) 2,75 kg/t	An2(-1,4meq/g) 0,75 kg/t	An2(-1,4meq/g) 1,75 kg/t	An2(-1,4meq/g) 2,75 kg/t
	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%
C	69	70	74	72	73	72
O	28	27	24	26	25	26
Al	0,3	0,3	0,2	0,2	0,2	0,2
Si	0,5	0,5	0,3	0,3	0,3	0,4
Cl	0,4	0,4	0,5	0,5	0,5	0,5
K	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ca	1,0	0,9	0,6	0,6	0,6	0,7
I	0,6	0,5	0,5	0,5	0,5	0,5
Total	100	100	100	100	100	100

8.6 Dryness of the wet web

Figure 56 illustrates how cationic polymer has better drainage effect than the anionic An2 (-1.39 meq/g). It can also be observed that addition of starch into system influences dewatering rate increasingly. Overall levels are a slightly high, except those of starch level 15 kg/t. In this study, the addition level of chosen polymer has little effect on drainage.

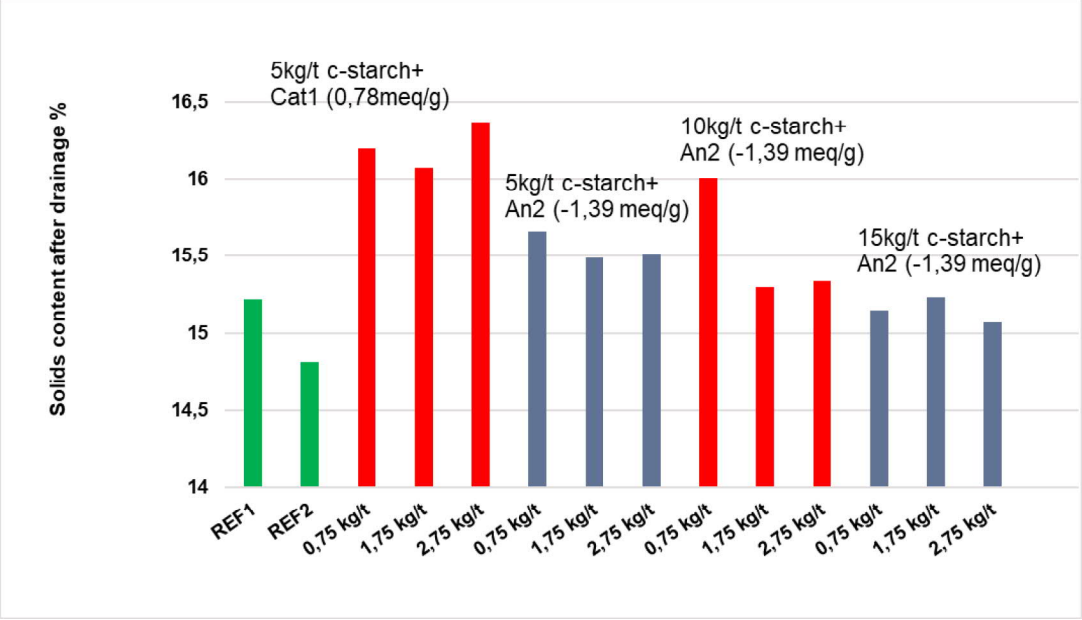

Figure 56. Solids content of the additional testing measured after drainage.

8.7 Statistical analysis of testliner measurements

Since the Z-directional tensile is the matter of importance in this study, the outcome of tensile results is approached with more detailed manner. Overall correlation of variants is also discussed.

8.7.1 Regression analysis of Z-directional tensile and bulk

Bulk is known to have strong relationship with the strength properties. *Figure 57* depicts the linear regression between bulk and Z-directional tensile. Bulk is seen as the explanatory variable for Z-directional strength. It can be seen from the negative slope, that the increase of bulk decreases Z-directional strength. Bulk correlates Z-directional strength more at lower bulk values, as the data points are situated closer to the regression line. The cationic data points, marked with red circle, loose strength when bulk is increased. Also, excess amount of cationic starch with high polymer addition level does not support strength formation.

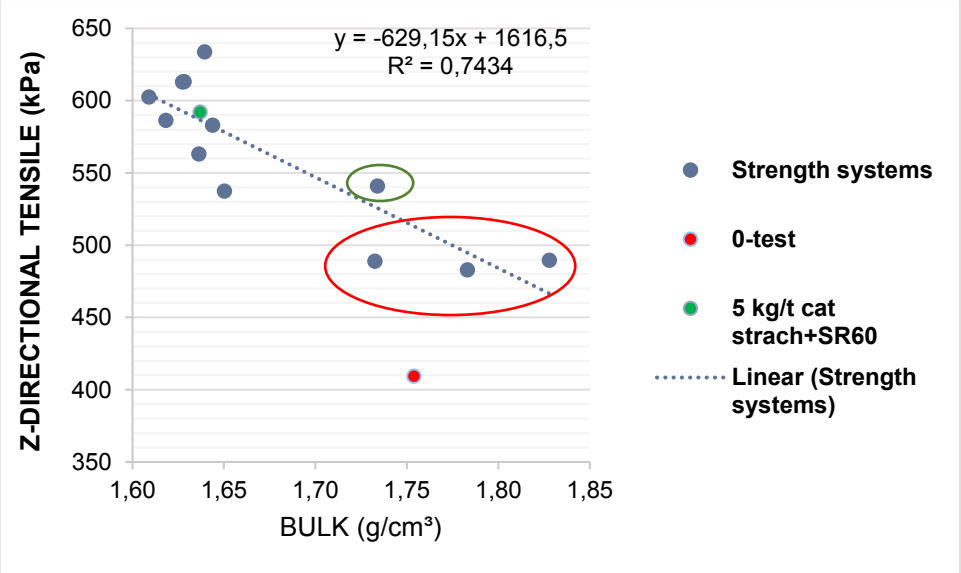

Figure 57. Regression analysis of Z-directional tensile versus bulk measured from additional test points.

Figure 58 depicts opposite situation between variables. Positive slope suggest that increase in bulk promotes compression. Cationic reference benefits greatly from bulk increase. The test points with denser sheets are left with lower compression. According to literature, denser sheets should result in greater compression. It its possible that excess number of cationic ions hinder bonding between fibers.

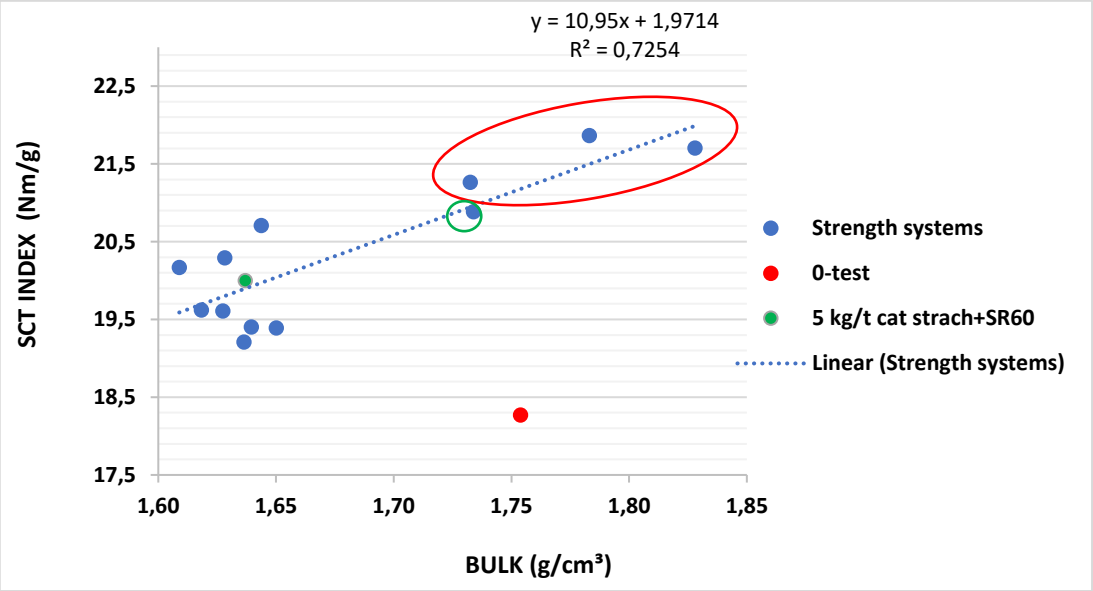

Figure 58. Linear regression of the additional SCT strength and measured bulk

At *table 12*, the R square (regression coefficient) informs, that bulk has more than 6 0 % effect on Z-directional strength. This indicates quite strong correlation between bulk and Z-directional strength. P-value < 0.05 indicates, that the results are statistically significant.

Table 12. Regression statistics on additional linerboard bulk and Z-strength measurements

Regression Statistics					
Multiple R	0,820913075				
R Square	0,673898276				
Adjusted R Square	0,648813528				
Standard Error	36,9892097				
Observations	15				
ANOVA				α=0,05	
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	36756,5472	36756,5472	26,8648614	0,00017619
Residual	13	17786,6212	1368,20163		
Total	14	54543,1684			
	Coefficients	*tandard Erro*	*t Stat*	*P-value*	
Intercept	1765,938985	233,979429	7,54741129	4,2056E-06	
Bulk	-723,288106	139,546524	-5,18313239	0,00017619	
	Lower 95%	*Upper 95%*	*Lower 95,0%*	*Upper 95,0%*	
Intercept	1260,45716	2271,42081	1260,45716	2271,42081	
Bulk	-1024,76004	-421,816171	-1024,76004	-421,816171	

9 CONCLUSIONS AND DISCUSSION

The purpose of the study was to examine the possibility to produce reliably multiply board sheets and testliner sheets in laboratory environment, using modern strength improving technologies. At the same time the aim was to find suitable combinations of Z-strength enhancing polymer combinations. The study showed, that dynamic sheet former allows the use of spray starch in FBB forming, additionally aqualayer was possible to include in testliner. While it is possible to prepare 3-ply sheets, it must be noted that the conditions where sheets are formed have great effect on the success of sheet making. The FBB sheets involve many layers and chemicals. In this study the time consumed in single sheet forming has most likely been too long, which might have had effect on the chemical performance and hence, the results. The biggest issue with testliner was the blocking of wire. In time, fines and small particles of RFC blocked the wire, which was very demanding to clean. Because of this, the test sheets made during time begun to hold more fines and particles, which affected the formation, solid contents and composition of the sheets.

Nevertheless, promising products were recognized. The Z-directional strength of FBB was improved by ~23 % compared to Ref 0, with combination of 5 kg/t cationic starch and slightly anionic 0.75 kg/t of Amph1 (-0.2 meq/g). Relatively low addition of polymers combined with low starch level is economically beneficial. Also, less starch will get to circulation. Both grades, FBB and testliner benefit from An2 (-1.4 meq/g). The Z-tensile of FBB with combinations of 0.75 kg/t strength polymer and 10 kg of cationic starch was improved by 16 %. Refined pulp alone gave strength to testliner 41 %. Introducing 15 kg/t cationic starch and 0.75 kg/t An2 (-1.4 meq/g) to the system, gave additional ~10 % increase in strength. Interesting is, that contrary to expectations anionic polymer gave opposite relationship between bulk and strength measurements. Despite the bulk increase, SCT was found to improve. Z-directional strength decreased with bulk increase. Nevertheless, increase in Z-directional strength was not gained with the cost of other strength parameters. Also, moderate increase in burst strength was observed. Although, An2 (-1.4 meq/g) had the greatest viscosity compared to other products, it is not an obstacle. Strength polymer in question is rather efficient also in lower quantities.

10 FUTURE RECOMMENDATIONS

During experimental part it was observed, that the thinner top layers of FBB and testliners were very sensitive against the pressure caused by spraying. It would be worthwhile investigating a separate tank and spraying system for the spray starch and aqualayer. I suggest a separate removable system with tank, mixer and a spraying bar with flat nozzles. This would minimize the spraying time and additionally, reduce the pressure effect of spraying towards wet web. Also, the time consumed in sheet making would be reduced. It would better simulate the actual paper making process allowing better quality sheets.

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Appendices

Appendix 1. Measurements of FBB preliminary tests

Appendix 2. Measurements of FBB additional tests

Appendix 3. Measurements of preliminary tests of testliner

Appendix 4. Measurements of additional tests of test iner

Appendix 1 (1). Measurements of FBB preliminary tests.

Measurement		REF0	REF1	An1 (-0,65 meq/g) 0,75kg/t	An1 (-0,65 meq/g) 1,5kg/t	An2(-1,4meq/g) 0,75kg/t
SC after drainage	%	14,4	14,7	13,3	15,5	15,8
SC after press	%	54,3	53,3	53,7		53,7
Grammage	g/m2	224,1	230,5	215,8	216,6	233,8
St.dev.	g/m2	0,78	0,08	0,10	0,42	0,06
95% confidence		1,09	0,09	0,11	0,48	0,07
Thickness	µm	549,6	559,0	514,1	531,1	564,0
St.dev.	µm	13,6	17,4	15,3	15,2	21,2
95% confidence		8,4	10,8	9,5	9,4	13,1
Bulk	cm3/g	2,45	2,42	2,38	2,45	2,50
Scott Bond	J/m2	49,9	41,3	44,9	40,2	46,1
St.dev.	J/m2	4	3	2	9	15
95% confidence		3	2	1	5	9
Z-strenght	kPa	106,27	100,20	100,87	101,27	112,48
St.dev.	kPa	37,69	2,55	19,01	17,50	6,77
95% confidence		30,2	2,0	15,2	14,0	5,4

Appendix 1 (2). Measurements of FBB preliminary tests

An2(-1,4meq/g)	An3(-1,1meq/g)	An3(-1,1meq/g)	An4 (-2 meq/g)	An4 (-2 meq/g)	An5(-4 meq/g)	An5(-4 meq/g)
1,5kg/t	0,75kg/t	1,5kg/t	0,75kg/t	1,5kg/t	0,75kg/t	1,5kg/t
14,0 52,7	14,4 52,8	14,7 53,8	13,9 52,9	13,8 53,9	12,2 55,8	14,5 54,5
204,0	217,3	221,4	214,9	206,8	219,6	224,0
0,00	0,48	0,42	0,60	0,20	0,56	0,50
#NUM!	0,55	0,48	0,68	0,23	0,64	0,57
501,6	544,4	552,2	521,2	510,2	543,3	523,4
16,3	13,8	21,7	29,4	26,2	22,7	19,1
10,1	8,6	13,4	18,2	16,2	14,1	11,9
2,46	2,51	2,49	2,43	2,47	2,47	2,34
45,8	40,2	41,3	61,0	89,9	43,2	43,3
4	6	2	5	6	3	2
3	4	1	3	3	2	1
110,60	91,23	105,42	117,03	110,28	93,47	112,65
6,24	6,53	1,66	19,65	11,92	7,92	1,52
5,0	5,2	1,3	15,7	9,5	6,3	1,2

Appendix 1 (3). Measurements of FBB preliminary tests.

Cat1 (0,8 meq/g)	Cat1 (0,8 meq/g)	Amph1(-0,2 meq/g)	Amph1(-0,2 meq/g)	Amph2(0,2 meq/g)	Amph2(0,2 meq/g)
0,75kg/t	1,5kg/t	0,75kg/t	1,5kg/t	0,75kg/t	1,5kg/t
14,0 52,4	14,1 54,6	14,2 51,9	16,9 51,2	14,6 56,6	14,2 54,4
221,6	221,7			219,99	
1,35	0,98			1,31	
1,52	1,11			1,11	
547,9	545,5			539,3	
32,9	25,4			20,2	
20,4	15,8			15,8	
2,47	2,46			2,45	
52,2	48,5	47,2	53,3	46,9	50,1
7	7	4	5	10	6
4	4	2	3	6	3
121,25	98,95	130,48	118,63	96,13	117,75
7,94	15,44	11,02	17,41	13,64	15,55
6,3	12,4	8,8	13,9	10,9	12,4

Appendix 2. Paper measurements of FBB additional tests.

Measurement	Standard		REF 0	REF1	An2(-1,4 meq/g) 0,4 kg/t	An2(-1,4 meq/g) 0,75 kg/t	An2(-1,4 meq/g) 1 kg/t
Grammage	ISO 536	g/m2	209,4	213,6	211,9	216,1	216,3
St.dev.		g/m2	2,63	1,15	1,44	1,57	1,25
95% confidence			2,98	1,3	1,63	1,78	1,41
Thickness	ISO 534	µm	513,08	544,78	510,98	512,42	522,61
St.dev.			15,52	24,27	17,68	16,15	18,39
95% confidence			7,85	12,28	8,95	8,17	9,31
Bulk	ISO 534	cm3/g	2,45	2,56	2,42	2,38	2,39
Scott Bond	T 569	J/m2	47	51	50	52	57
St.dev.		J/m2	2	5	2	8	6
95% confidence			1	3	1	4	3
Z-strenght		kPa	100,5	95,8	113,5	130,8	122,4
St.dev.			10,6	5,3	6	17	9,7
95% confidence			6,91	3,47	3,91	11,14	6,32
SC after drainage			14,7	14,5	14,9	14,8	14,9
SC after press			52	57,1	54,7	52,8	52,6

Measurement	Standard		Amph1(-0,2 meq/g) 0,4 kg/t	Amph1(-0,2 meq/g) 0,75 kg/t	Amph1(-0,2 meq/g) 1 kg/t
Grammage	ISO 536	g/m2	213,6	213,6	205,9
St.dev.		g/m2	1,32	1,82	1,24
95% confidence			1,5	2,06	1,4
Thickness	ISO 534	µm	507,83	498,53	502,57
St.dev.			17,06	18,77	17,44
95% confidence			8,64	9,5	8,82
Bulk	ISO 534	cm3/g	2,39	2,43	2,44
Scott Bond	T 569	J/m2	49	52	50
St.dev.		J/m2	6	6	1
95% confidence			3	3	0
Z-strenght		kPa	114	114,1	113,7
St.dev.			8,1	2,8	6,8
95% confidence			5,3	1,8	4,47
SC after drainage			15	14,7	15,4
SC after press			54,3	54	52,9

Appendix 3 (1). Measurements of preliminary tests of test liner

		Ref 1	Ref2	An4 (-2 meq/g)			An6(-0,55meq/g)		
	REF 0	ONLY SR60	starch 15kg/t	1kg/t	2kg/t	3kg/t	1kg/t	2kg/t	3kg/t
SC after drainage	14,5	15,19	15,79	15,78	14,68	14,56	14,74	15,69	13,97
Grammage	110,9	114,2	115,8	121,2	118,6	121,6	112,9	118,6	111,6
Thickness	198,7	196,3	195,6	203,9	199,1	203,1	201,0	190,1	193,9
Stdev	4,8	2,8	1,7	5,1	3,1	3,1	3,4	7,2	2,1
95% conf	3,29	1,96	1,21	3,51	2,17	2,16	2,32	5,01	1,47
Bulk	1,79	1,72	1,69	1,68	1,68	1,67	1,78	1,77	1,74
SCT CD	1,38	1,35	1,49	1,55	1,61	1,60	1,47	1,31	1,38
Stdev	0,10	0,07	0,26	0,09	0,14	0,06	0,07	0,12	0,03
95% conf.	0,05	0,03	0,14	0,05	0,10	0,03	0,03	0,06	0,01
SCT CD index	12,43	11,82	12,83	12,77	13,57	13,12	12,98	11,06	12,39
SCT MD	2,57	3,11	3,31	3,35	3,35	3,50	3,07	2,87	3,11
Stdev	0,32	0,15	0,16	0,14	0,16	0,20	0,22	0,27	0,10
95% conf.	0,19	0,07	0,08	0,08	0,08	0,10	0,12	0,16	0,05
SCT MD index	23,18	27,27	28,59	27,67	28,26	28,81	27,19	24,19	27,90
SCT GM index	16,97	17,95	19,15	18,80	19,58	19,44	18,79	16,35	18,59
Z-strength	375,12	412,74	525,18	491,06	543,40	546,06	522,60	542,38	526,90
Stdev	24,14	7,11	25,26	37,62	28,59	16,27	26,30	23,65	41,40
95% conf	21,16	6,23	22,14	32,98	25,06	14,26	23,05	20,73	36,29
Ash	13,1	13,6	14,1	13,9	13,8	14,2	13,2	13,4	13,6
Burst	234,89	247,04	277,43	286,60	292,79	308,01	275,87	258,98	261,72
Stdev	16,54	12,74	12,42	11,10	18,58	13,83	7,46	15,30	9,10
Burst index	2,12	2,16	2,40	2,36	2,47	2,53	2,44	2,18	2,34
95% conf.	11,46	8,83	8,60	7,69	12,87	9,58	5,17	10,60	6,30

Appendix 3 (2). Measurements of preliminary tests of test liner

An2(-1,4meq/g)			Amp3(-0,2meq/g)			Amph4(0,2 meq/g)		
1kg/t	2kg/t	3kg/t	1kg/t	2kg/t	3kg/t	1kg/t	2kg/t	3kg/t
14,81	16,35	16,08	16,04	14,54	15,06	15,05	15,36	13,83
121,6	117,9	114,8	118,9	117,8	118,5	115,9	122,1	118,4
207,0	201,8	198,5	203,4	198,7	200,9	200,9	210,6	202,7
2,1	4,7	2,4	2,6	1,5	2,3	3,5	7,6	3,2
1,47	3,29	1,69	1,81	1,06	1,61	2,44	5,25	2,23
1,70	1,71	1,73	1,71	1,69	1,70	1,73	1,72	1,71
1,57	1,62	1,53	1,48	1,50	1,50	1,38	1,50	1,48
0,07	0,05	0,07	0,03	0,06	0,11	0,07	0,03	0,05
0,03	0,02	0,03	0,01	0,03	0,05	0,04	0,01	0,03
12,88	13,74	13,30	12,49	12,75	12,68	11,88	12,26	12,48
3,42	3,45	3,23	3,35	3,29	3,39	3,13	3,21	3,05
0,17	0,14	0,16	0,16	0,15	0,18	0,20	0,27	0,19
0,08	0,09	0,11	0,11	0,10	0,12	0,14	0,18	0,13
28,12	29,29	28,16	28,14	27,97	28,62	27,02	26,27	25,72
19,03	20,06	19,35	18,74	18,88	19,05	17,91	17,94	17,91
555,74	566,72	565,74	501,88	528,78	511,52	477,36	505,84	499,44
24,13	21,54	23,41	29,39	21,98	17,95	8,35	22,74	17,04
17,88	18,88	20,52	25,77	19,27	15,73	7,32	19,93	14,94
13	12,9	12,1	13,9	13,3	12,8	13,5	14,2	14,1
302,71	297,27	285,71	280,59	276,47	282,52	263,53	270,36	271,64
9,78	16,52	12,44	8,76	22,71	15,52	11,28	34,58	7,87
2,49	2,52	2,49	2,36	2,35	2,38	2,27	2,21	2,29
6,78	11,45	8,62	6,07	15,73	10,76	7,81	23,96	5,45

Appendix 4 (1) Additional tests of test liner

	REF0	ONLY (SR 60) REF1	5 kg/t cat strach+SR60 REF2	5 kg/t c-starch+Cat1 (0,78meq/g) 0,75 kg/t	1,75 kg/t	2,75 kg/t	5kg/t c-starch+An2(-1,39meq/g) 0,75 kg/t	1,75 kg/t	2,75 kg/t
SC after drainage	16,36	15,22	14,81	16,2	16,07	16,37	15,66	15,49	15,51
SC after press	61,29	56,95	57,76	57,76	57,14	59,67	57,74	56,9	57,89
Grammage	110,5	116,2	101,6	105,7	104,3	106,6	109,4	105,1	104,5
Thickness	193,8	187,0	166,3	183,1	190,7	190,1	180,5	172,0	171,8
Stdev	6,9	3,1	3,4	3,6	4,3	6,0	3,0	1,4	2,7
95% conf	4,28	1,92	2,08	2,24	2,68	3,73	1,86	0,86	1,70
Density	0,57	0,62	0,61	0,58	0,55	0,56	0,61	0,61	0,61
Bulk	1,75	1,61	1,64	1,73	1,83	1,78	1,65	1,64	1,64
SCT CD	1,39	1,58	1,45	1,52	1,60	1,56	1,51	1,45	1,50
Stdev	0,10	0,08	0,06	0,10	0,08	0,24	0,07	0,07	0,04
95% conf.	0,05	0,04	0,03	0,05	0,04	0,12	0,03	0,03	0,02
SCT CD index	12,58	13,56	14,23	14,37	15,30	14,60	13,84	13,77	14,35
SCT MD	2,93	3,18	2,85	3,32	3,21	3,49	2,97	2,82	3,12
Stdev	0,18	0,28	0,19	0,09	0,71	0,20	0,23	0,21	0,12
95% conf.	0,09	0,14	0,10	0,05	0,36	0,10	0,12	0,11	0,06
SCT MD index	26,52	27,39	28,10	31,45	30,78	32,73	27,17	26,80	29,88
SCT GM index	18,27	19,28	20,00	21,26	21,70	21,86	19,39	19,21	20,70
Z-strength	409,28	577,98	592,03	488,75	489,45	482,77	537,37	563,10	582,92
Stdev	46,44	51,84	49,35	46,16	28,10	46,44	57,07	38,83	14,26
95% conf	37,16	41,48	39,49	36,93	22,48	37,16	45,67	31,07	11,41
Ash	12,63	12,39	12,89	11,8	13,36	13,36	12,42	13,03	13,6
Burst	230,85	279,55	270,76	234,74	255,44	243,38	294,47	286,08	269,12
Stdev	6,14	27,70	10,04	13,74	25,64	20,00	9,80	11,47	10,74
Burst index	2,09	2,41	2,66	2,22	2,45	2,28	2,69	2,72	2,58

Appendix 4 (2) Additional tests of test liner.

10kg/t c-starch+ An2(-1,39meq/g)			15kg/t c-starch+ An2(-1,39meq/g)		
0,75 kg/t	1,75 kg/t	2,75 kg/t	0,75 kg/t	1,75 kg/t	2,75 kg/t
16,01	15,3	15,34	15,15	15,23	15,07
58,01	54,97	55,35	56,15	54,97	53,49
108,6	108,0	107,5	108,4	100,8	108,9
175,8	173,8	174,9	177,7	164,1	188,8
1,9	3,2	2,5	5,6	1,9	3,9
1,18	1,98	1,55	3,48	1,20	2,40
0,62	0,62	0,61	0,61	0,61	0,58
1,62	1,61	1,63	1,64	1,63	1,73
1,52	1,55	1,52	1,56	1,49	1,56
0,08	0,06	0,10	0,06	0,16	0,09
0,04	0,03	0,05	0,03	0,08	0,05
14,00	14,33	14,10	14,40	14,76	14,35
2,99	3,07	2,93	2,83	2,81	3,31
0,13	0,13	0,21	0,76	0,09	0,23
0,07	0,06	0,10	0,39	0,04	0,12
27,50	28,38	27,26	26,14	27,89	30,39
19,62	20,17	19,61	19,40	20,29	20,88
586,33	602,47	612,83	633,82	613,05	540,90
43,49	39,81	38,71	44,20	39,84	27,90
34,80	31,85	30,97	35,37	31,88	22,32
11,87	11,5	12,4	12,82	13,7	13,34
288,55	293,75	301,24	297,61	257,24	262,38
13,99	15,24	14,33	8,73	35,42	28,84
2,66	2,72	2,80	2,75	2,55	2,41
9,69	10,56	9,93	6,05	24,54	19,98